Chemistry | Lancaster University

Low energy water quality monitoring of toxic metals

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Abstract

Isotachophoresis (ITP) has been investigated as a potential on-line instrument to measure water quality in the industry. The project focused on the following ions: Al^{3+}, Ca^{2+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Mg^{2+}, NH_4^+, and Pb^{2+}. The choice of ions was made by the sponsor company Process Instruments Ltd, which was looking to design the prototype instrument based on ITP separation. A number of methods from the literature were evaluated and were studied further. That included preparation of calibration graphs which were used in calculations of the ions concentrations, experiments at various pH of the electrolytes, comparison of the results with conventional separation techniques such as: ion chromatography (IC) and inductively coupled – optical emission spectrometry (ICP-OES).

The number of samples analysed was: 8 samples of commonly available bottled water and 13 tap water samples from around the Europe, including samples from: Poland. Greece, France, Turkey and many locations in the UK.

In the project nine different ITP electrolyte systems were investigated, number of them allowed separation of multiple ions of interest. ICP-OES experiments included analysis of samples at various wavelengths (each element was analysed at 6-12 different wavelengths). IC column available at the university only allowed separation of calcium, magnesium and ammonium ions.

The final stage of the project included design and construction of the prototype instrument. In the end it was possible to construct the prototype of instrument based on ITP separation. The system was set up using parts widely available in every laboratory, syringes, plastic tubing and platinum wire. It reused the power supply which was used in different projects. The detector was designed and made by the supervisor especially for this project. The prototype has been proven to be working by the separation of the anionic dyes, bromophenol blue and amaranth using electrolytes system consisting of leading electrolyte: 10mM HCl, 0.05% Mowiol, pH 6.0 (adjusted by histidine) and terminating electrolyte: 10mM MES, pH 6.0 (adjusted by histidine) with applied voltage of 3500V. Unfortunately the timescale of the project prevented further optimisation and evaluation of the prototype, it left the exciting part of the process for the sponsor company.

Declaration

No portion of this work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

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Table of Contents

List of figures

List of tables

Glossary

α-CD	α-cyclodextrin
β-CD	β-cyclodextrin
γ-CD	γ-cyclodextrin
15-c-5	15-crown-5
18-c-6-e	18-crown-6-ether
Ac	Acetate
ACES	N-(2-Acetamido)-2-aminoethanesulfonic acid
ADA	N-(2-acetoamido)-iminodiacetic acid
Ala	L-alanine
AMIM	1-n-amyl-3-methyl-imidazolium cation
Ammediol	2-amino-2-methyl-1,3-propanediol
AMPA	Aminomethylphosphonic acid
Asp	L-aspatric acid
BALA	β-alanine
BICINE	N,N-Bis(2-hydroxyethyl)glycine
BMIM	1-butyl-3-methyl-imidazolium cation
BTP	1,3-bis[tris(hydroxylmethyl)methyl-amino]propane
CAA	Cyanoacetic acid
Car Hydro	(±)-Carnitine hydrochloride
CCC	Chloromequat
CITR	Citric acid
CON	Conductivity detector
CON CON	Contact conductivity detector
DAP	1,3-diaminopropane
DCTA	Trans-1,2-Diaminocyclohexane-N,N,N',N'-tetraacetic acid
Den	Diethylene triamine
DME	1,2-dimorpholinylethane
DMF	N,N-Dimethylformamide
DOTA	1,4,7,10-Tetraazacyclododecane-1,4,7,10-tetraacetic acid

DTPA	Fiethylenetriaminepentaacetic acid
EACA	ε-aminocaprocic acid
EDA	Ethylenediamine
EDTA	Edetic acid
EtG	Ethyl-β-D-6-glucuronic acid
GABA	γ -amino-n-butyric acid
Glu	L-glutamic acid
Gly	Glycine
HAc	Acetic acid
HEC	Hydroxyethylcellulose
HEPES	4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid
HFG	Halofuginone ((+/-)-trans-7-bromo-6-chloro-3-(3-(3-hydroxy-2-piperidyl)-acetonyl)-4(3H)-quinazolinone)
HIBA	Hydroxyisobutyric acid
HIDA	N-hydroxyethyliminodiacetic acid
His	Histidine
HMIM	1-n-hexyl-3-methyl-imidazolium cation
HPC	Hydroxypropylcellulose
HPMC	Hydroxypropylmethylcellulose
IDS	Iminodisulfonate
IP5	Inositol pentaphosphate
IP6	Phytic acid
LE	Leading electrolyte
MES	2-[n-morpholino]ethansulpfonic acid
MHEC	Methylethlhydroxyl-cellulose
MMAT	Mouse monoclonal antibodies against porcine transferrin
MOPS	3-(*N*-morpholino)propanesulfonic acid
Mowiol, PVA	Poly(vinyl alcohol)
MPP	Methylphosphinicopropionic acid
NH_4Pic	Ammonium picolinate
NON CON	Contactless conductivity detector

NR_4^+	Quaternary ammonium salt
OMIM	1-n-octyl-3-methyl-imidazolium cation
PDTA	1,2-Diaminopropane-N,N,N',N'-tetraacetic acid
PEG	Polyethyleneglycol
Phe	L-phenylalanine
PHO	Photometric detector
PIXE	Particle induced X-ray detector
PMIM	1-n-propyl-3-methyl-imidazolium cation
POT	Potential detector
PVA, Mowiol	Poly(vinyl alcohol)
PVP	Polyvinylpyrrolidone
SPH	Spectrophotometric detector
TBA	Tetrabuytlammonium hydroxide
TE	Terminating electrolyte
TEA^+	Tetraethylammonium
TETA	Triethylenetetramine
THE	Thermal detector
TMOH	Tetramethylammonium hydroxide
Tris	Tris(hydroxymethyl)aminomethane
UV	Ultra-violet spectrometric detector
Val	L-valine

Chapter 1 Introduction

1.1 Aims of the project

This research programme is concerned with the separation technique of isotachophoresis applied to the separation, determination and quantitation of the concentrations of a list of ionic species of key importance in the water industry. Some of these highlighted ions need to be monitored purely on the basis of their toxicity and consequent potential threat to health. Within this project, Cu^{2+}, Cr^{3+}, and Pb^{2+} fall into this category. Other ions are specifically associated with the process of coagulation control used in the process of water purification and the removal of unwanted particulates (Al^{3+} and Fe^{2+}). They are used as coagulation reagents. $NH_4^+$is another important ion that requires identification and quantitation due to the possible effect on health with long lasting results. Finally, Mg^{2+} and $Ca^{2+}$are important as key ions in the definition of water hardness.

The technique of isotachophoresis, although as yet not employed as an on-line or at-line measurement instrument within the water industry, has a number of potential advantages that could be regarded as commercially attractive. The instrumentation is simple in that the separation process is confined to ionic migration, alone, within a generic capillary tube the material of which plays no part in the separation process. The separation chemistry is usually based on relatively simple electrolyte formulations that have longevity of months, and so are suitable for a well-spaced maintenance schedule, if used in a remote location. The quantitation in isotachophoresis is based upon time intervals between contiguous separated zones, such that the detector does not need to be calibrated, nor does is the detector required to have a particularly linear transfer function with respect to concentration. This is a particularly attractive feature since most field-based wet-chemical analysers are prone to problematic detection calibration. Finally, the waste produced is usually of low toxicity. The only major drawback is the need to apply high voltage separation fields (usually in the range of 1 to 10kV). This project has been an industrial PhD programme, co-sponsored by Process Instruments Ltd. who are an established, but growing SME based in the NW town of Burnley. They supply measurement and control instrumentation to both the drinking water and waste water industries, and specialise in disinfection process control and partial removal through the measurement and control of coagulation chemistry. The ions listed above have been chosen by the sponsoring company as key target ions that are currently difficult to measure using on-line or at-line instrumentation. The interest in ITP is to understand its potential as an

instrumentation platform that could assist in the determination of these ions within a remote access situation, and also to assess the potential commercial opportunity in the application of isotachophoresis in new concept chemical measurement instrumentation.

There are three principal aims to this research programme:

1. To investigate exhaustively the literature-reported methodologies where isotachophoresis has been used within a laboratory environment to separate and measure the ions of interest that have been identified by the sponsoring company.
2. To thoroughly evaluate the most promising electrolyte systems found in the first principal aim, to optimise the electrolyte chemistry for the concentration ranges relevant to the water industry for each highlighted ion. And, where necessary to develop novel electrolyte chemistries for isotachophoretic separation, either because such systems have not been reported in the literature, or where literature-reported electrolyte chemistries fall short of the industry requirements.
3. To systematically design and develop a research prototype isotachophoretic instrument, that demonstrates the feasibility of applying a robust isotachophoresis instrument within the working environments associated with the water industry.

An additional aim set by the company was trial the prototype instrument on site, but this was not feasible due to the severe restrictions imposed during the Covid 19 pandemic, which spanned the latter half of this research programme. The ideal prototype instrument should be based on the principle of ITP to replace current commercial instruments. These are usually based upon a wet-chemical reagent-based reaction that is monitored by in-line spectrophotometry[1–3]. Any replacement device should be cheap and easy to use, based on longer shelf-life reagents than used for spectrophotometry. This will result in the reduction of liquid chemical waste to approximately 5% of the current waste production. The designed prototype instrument should require less maintenance visits and use longer shelf-life chemicals and thus reduce chemical waste.

1.2 Ions analysed during the PhD project

Initially six ions, Al^{3+}, NH_4^+, Cu^{2+}, Cr^{3+}, Pb^{2+} and Fe^{2+}, were investigated in the project. Later, Ca^{2+} and Mg^{2+} were added due to these being of interest of the sponsor company. All of these ions occur naturally in water however, their concentrations are strictly controlled during water treatment.

According to Drinking Water Standards the concentration should not exceed: 200µg/l of aluminium, 0.5 mg/l of ammonium, 50 µg/l of chromium (including all chromium ions), 2.0 mg/l of copper, 200 µg/l of iron II and III, and 10 µg/l of lead[4].

Exposure to high level of aluminium dust may cause Alzheimer's disease and lungs problems such as coughing or changes that show up in chest X-ray[5].

Chronic inhalation of excessive concentrations of iron oxide fumes or dusts may result in development of a benign pneumoconiosis, called siderosis, which is observable as an x-ray change, it may also increase the risk of lung cancer. A more common problem for humans is iron deficiency, that leads to anaemia[6].

Long-term contact with ammonia and ammonium ions results in coughing, bronchospasm and chest pain along with severe eye irritation and tearing. At higher concentrations it causes chemical bronchitis, fluid accumulation in the lungs or chemical burns[7].

Chromium VI is much more harmful to health than chromium III, however chromium III also causes irritation to respiratory tract such as: asthma, cough, shortness of breath or wheezing[8].

Copper is essential to good health but higher levels of copper in drinking water may cause nausea, vomiting, stomach cramps or diarrhoea, long-term intake of copper can cause liver and kidney damage or even death[9].

Lead exposure may affect the nervous system and cause weakness in fingers, wrists or ankles, and an increase in blood pressure or anaemia. At higher levels, lead can severely damage brain and kidneys, and may cause miscarriage or affect male reproduction system[10].

Calcium and magnesium salts (carbonates, bicarbonates, chlorides, sulphates and nitrates) are responsible for water hardness[4,11]. Hard water causes scaling in hot water systems such as: kettles, electronic irons and domestic appliances. On the other hand, soft water will have a low buffering capacity, and thus is more corrosive to pipes. Scaling of heating elements shortens their life and makes appliances less effective. There is no health-based standard for water hardness of drinking

water, however The World Health Organisation Guidelines 2004 stated that a hardness value of 200 mg/l or higher will produce scale. Soft water with value of 100 mg/l or less will be more corrosive to pipes. The recommended concentration of calcium and magnesium ions is 250 mg/l.

Chapter 2 Isotachophoresis (ITP) as a separation technique

2.1 Isotachophoresis (ITP)

Isotachophoresis (ITP) is an electrophoretic separation technique that separates ions, based on their electrophoretic mobility within a supporting electrolyte. The chemistry of the electrolyte plays a key role in the definition of the electrophoretic mobility of a given ion in a given chemical environment. Unlike capillary electrophoresis, ITP generates separated zones of equal concentration, such that adjacent zones are contiguous. Detection in unusual, in that it is the length of a separated zone, rather than any peak response, that defines the quantitation.

In isotachophoresis, two electrolytes are used, a leading (LE) and a terminating (TE) electrolyte. The principle for choosing electrolytes is: the primary leading electrolyte ion has a higher mobility and the primary terminating electrolyte ion has a lower mobility than any of the ion species in the separated sample[12,13]. Samples are injected in between the LE and TE as shown in Figure 2-1a. When an electric current is applied to the system, ions begin to separate and organise themselves in order of decreasing mobility (Figure 2-1b). Figure 2-1c presents a completed separation. The mobilities of sample are: $\mu_{LE}>\mu_A>\mu_B>\mu_C>\mu_{TE}$ where μ is electrophoretic mobility. This may be carried out at constant voltage or constant current[14,15].

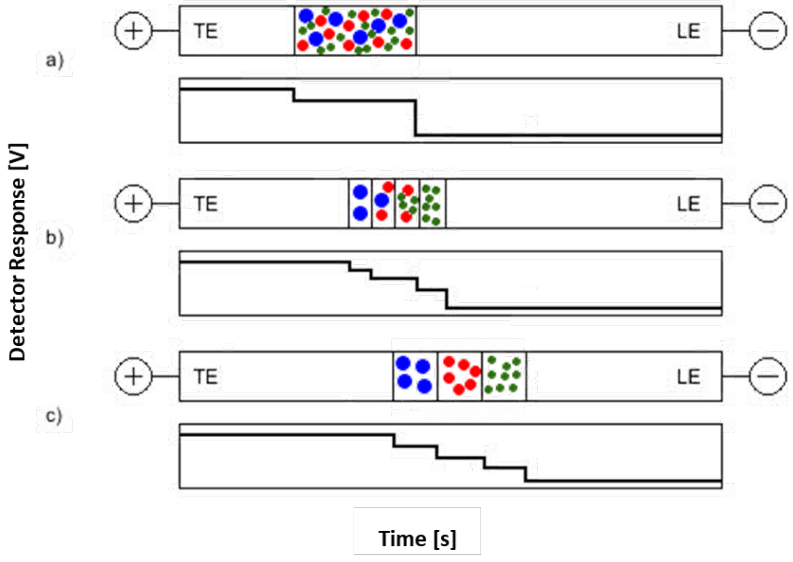


Figure 2-1: Presentation of isotachophoresis separation with analysis results. ● is sample ion A, ● is sample ion B and ● is sample ion C, LE is leading electrolyte and TE is terminating electrolyte. a) presents system at the beginning of analysis, just after sample injection, b) ions during separation and c) separated ions.

2.1.1 **Mobility**

Electrophoretic mobility (μ_{EP}) $\left[\frac{m^2}{V \cdot s}\right]$ is the constant of proportionality between the velocity of the ion and the strength of the electric field. It is proportional to the charge of the ion and inversely proportional to the friction coefficient of the ion (in a given electrolytic environment). Electrophoretic mobilities of the ions analysed in the project are presented in Table 2-1.

Electrophoretic mobility is calculated:

$$\mu_{EP} = \frac{u_{EP}}{E} \qquad \text{(Eq 1)}$$

Where *E* is applied electric field $\left[\frac{V}{m}\right]$ and u_{EP} $\left[\frac{m}{s}\right]$ is the velocity of the ion.

The friction coefficient (*f*) [N] for a spherical ion can be calculated using Stoke's Law, where *r* is the radius [m] of the ion and η is the viscosity $\left[\frac{N \cdot s}{m^2}\right]$ of the supporting buffer:

$$f = 6 \cdot \pi \cdot \eta \cdot r \qquad \text{(Eq 2)}$$

Table 2-1: Electrophoretic mobilities of the ions analysed in this PhD project[15].

Ion	Mobility (*10^{-5}) [$cm^2V^{-1}s^{-1}$]
Al^{3+}	63.2
Ca^{2+}	53.2-61.6
Cr^{3+}	69.4
Cu^{2+}	47.0-54.5
Fe^{2+}	54.0-56.0
Mg^{2+}	48.2-55.0
NH_4^+	66.7-74.0
Pb^{2+}	70.0-73.6

2.1.2 **Data analysis**

The isotachopherogram of every analysis shows a series of steps (Figure 2-2). Each step corresponds to a different ion. The step height is the qualitative parameter and is characteristic of the analysed ion. The step length allows quantitative interpretation of the sample. The calibration graph for each

ion plots the step length against the concentration for an ion of interest. In principle, the step length is proportional to the concentration of the associated ion (or ion complex).

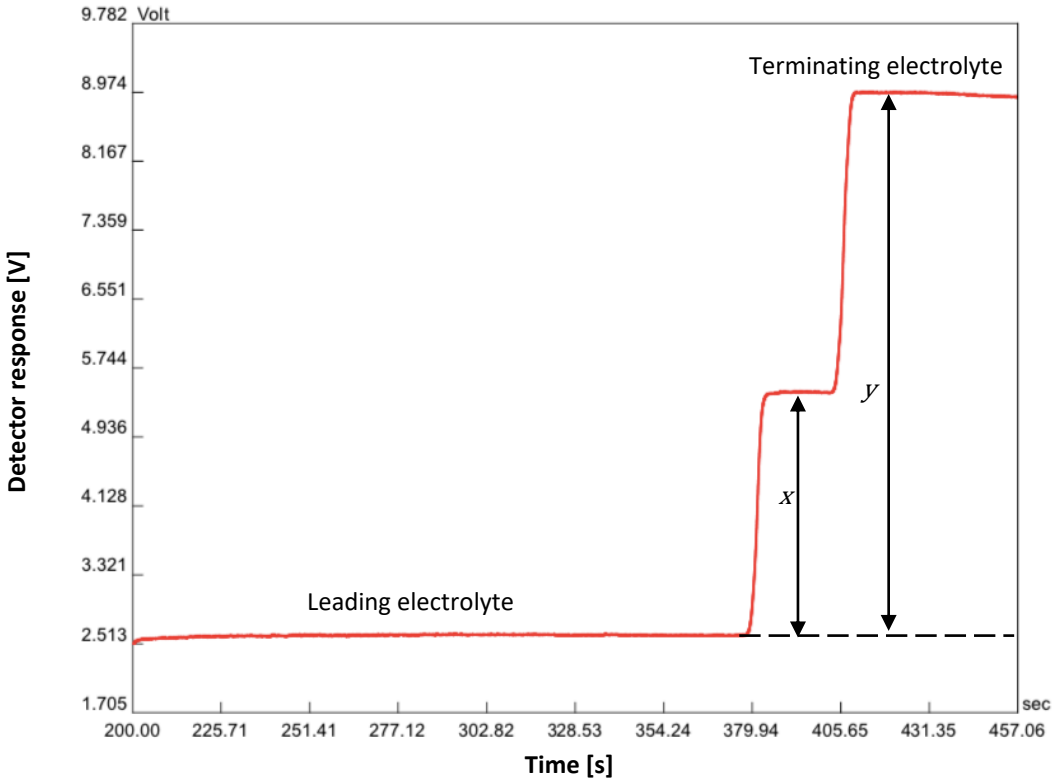


Figure 2-2: An example of an isotachopherogram.

Relative step height (RSH) is calculated as seen in (Eq 3. Where *x* and *y* are values taken from Figure 2-2.

$$RSH = \frac{x}{y} \qquad \text{(Eq 3)}$$

2.1.3 **Detectors available in isotachophoresis analysis**

The most common detectors used in isotachophoresis are conductivity and UV absorbance. However there is the possibility of using more specialised detectors if required, as outlined below. Limits of detection are calculated based on the isotachophoretic analysis of various samples.

Table 2-2: Reported limits of detection for detectors used in electrophoretic separations[16–22].

Detection system	Reported limit of detection (µg/L)
Conductivity	10-20
UV absorbance	10-100
Fluorescence	20-50
Mass spectrometry	0.3-0.5
Thermometric	20-50
Potentiometry	10-50

2.1.3.1 **Conductivity**

Conductivity is a widely used detection system in isotachophoretic separations. It can be performed using both, dc and ac techniques. The detector measures a potential between two electrodes while passing a small constant current. There are two types of conductivity detectors available, contact and contactless. Detailed description of the detector used in the project is available in section 2.1.10.

2.1.3.2 **UV absorption**

UV absorption may be used as a detection system in some separations. It is usually used coupled with another detection techniques usually with conductivity detector. That allows better identification of the exact position and thickness of the zone boundaries. The wavelengths mostly used are 254 and 280nm (usually used in analysis of proteins or organic compounds). Most of the separation tubes used in ITP are made of PTFE. Because of the PTFE usage of wavelengths below 230nm is impossible, due to the UV dispersion and absorbance by PTFE material.

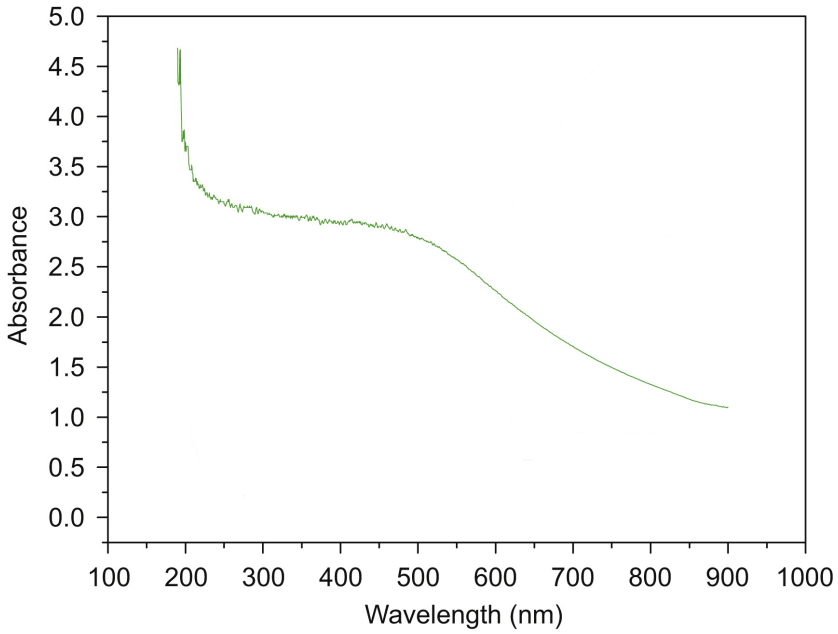


Figure 2-3: Light absorbance of PTFE[23].

2.1.3.3 **DAD (diode-array detector)**[24–28]

Unlike UV absorbance detectors, DAD is capable of detection using multiple wavelengths at the time. It detects absorption in UV to visible region. A light source used in system is a deuterium lamp, the grating is used to spread the light into various wavelengths. Which is then transmitted through the slit and passes through the flow cell. The amount of light transmitted to the photodetector is reduced and the difference in transmittance is converted into the detector output in absorbance units.

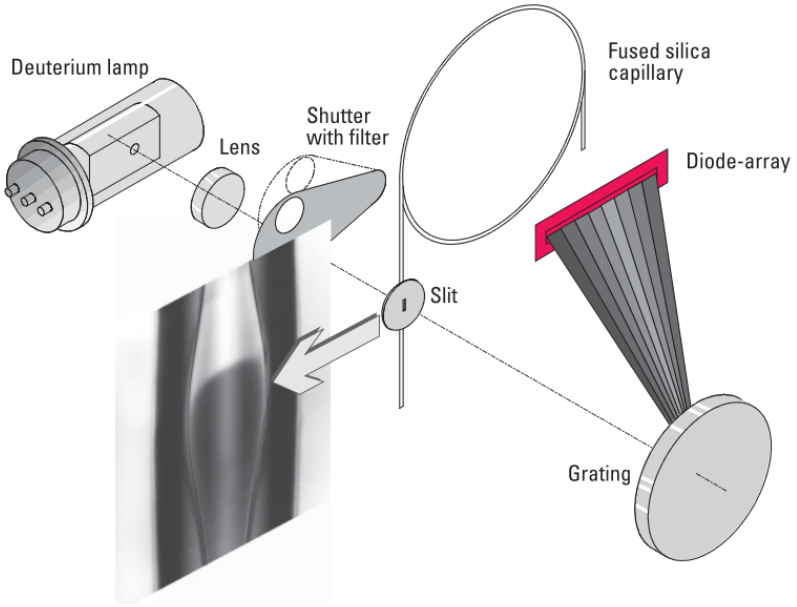


Figure 2-4: Schematic of on-capillary DAD detection system[25].

2.1.3.4 **Thermometric**[29]

In separation systems with stabilised electric current, the heat produced increases from front side towards the rear of the separation in a defined way. The separation zones are characterised by the sharp changes in temperatures. The changes correspond to the zone change. Thermometric detection provides both quantitative and qualitative information about the analysed sample. The temperature is measured with micro-thermocouples or micro-bead thermistors.

The main disadvantage of this detector is lack of high resolution as the heat generated by the electric field has to diffuse through the wall of the tube. All parts of the system must be thermally isolated to avoid false readings.

2.1.3.5 **Amperometric detection**[30]

This detection technique looks at the change of electric current in time. The current is produced by the oxidation or reduction of sample's components. It provides sensitivity and high selectivity to electroactive substances.

2.1.3.6 **Mass spectrometry**[22]

Mass spectrometry is particularly useful if qualitative characterisation of the samples is needed. It is highly sensitive but destructive technique thus it usually placed at the end of the capillary tube. This detection system is expensive and complicated to implement in the isotachophoretic systems. The electrolyte used in separation may interfere with the MS detector.

2.1.3.7 **Fluorescence**[19]

The fluorescence detector detects the optical emission of the fluorescent molecules. The disadvantages of using this type of the detector are: costs of the equipment, limited wavelengths of laser light and possible degradation of photosensitive samples due to the exposure to intense light. Detection of the non-fluorescent molecules is also available, however it requires additional sample treatment. One option is to add a fluorophore into the background electrolyte or to tag an analyte via pre-derivatisation in the sample preparation step.

2.1.4 Additives in the leading electrolyte

2.1.4.1 Electro-osmotic flow (EOF)

Electro-osmotic flow describes the movement of a liquid over a solid surface in the presence of a longitudinal applied electric field gradient. The inside wall of a fused-silica capillary is covered with silanol (Si–OH) groups with a negative charge ($Si–O^-$) above pH≈2[31]. The double layer consists of fixed negative charge on the wall and excess cations near the wall (diffused layer), as illustrated in Figure 2-5.

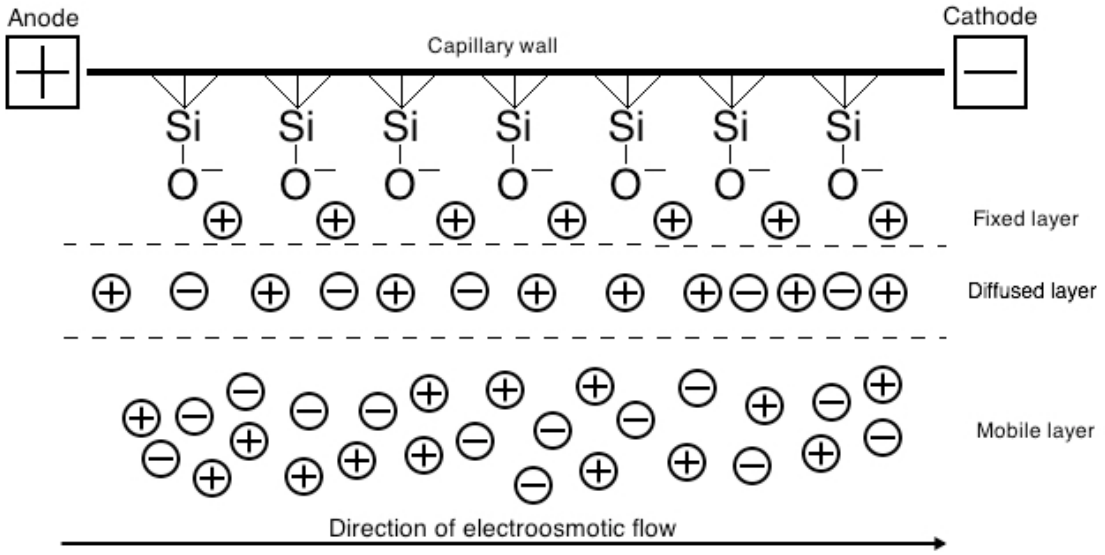


Figure 2-5: Schematic of electro-osmotic flow[32].

The electro-osmotic flow, v_{EO} may be described by the von Smolchowski equation:

$$v_{EO} = \left(\frac{\varepsilon\zeta}{4\pi\eta}\right)E \qquad \text{(Eq 4)}$$

Where ε is the dielectric constant, ζ is 'zeta' potential (the potential at the edge of the Stern layer), η is viscosity and *E* is electric field strength.

The zeta potential (ζ-potential) is the potential difference across phase boundaries between solids and liquids. It is a measure of the electrical charge of particles (in this case, ions) that are suspended in liquid (Figure 2-6)[14].

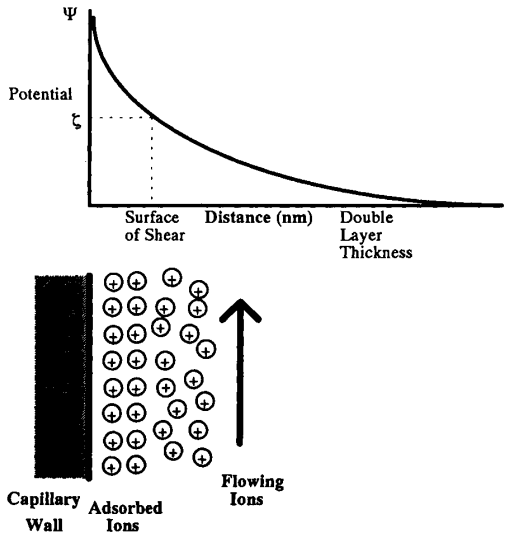


Figure 2-6: Zeta potential origin.

The thickness of the double layer (δ) ranges from ~10nm when ionic strength is 1mM to ~0.3nm when ionic strength is 1M, generally it increases with decreasing ionic strength. The double layer supports plug-like flow of the solution toward the cathode, which is called electro-osmotic flow (Figure 2-7).

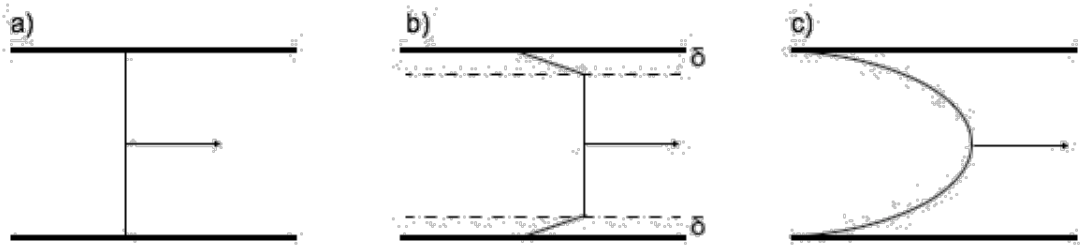


Figure 2-7: Different types of flow. a) theoretical plug flow, b) electroosmotic flow, c) laminar flow.

Examples of capillary materials which support electro-osmotic flow are: fused silica, glass, polyfluorocarbons (such as PTFE or FEP) and polyethylene. In discussed ITP system, fluorinated ethylene propylene (FEP) is used in the pre-separation column and quartz glass in the analytical column. The influence of buffer pH on the electro-osmosis for the three materials is shown in Figure 2-8. For all presented materials the rule is the higher pH, the higher electro-osmotic flow.

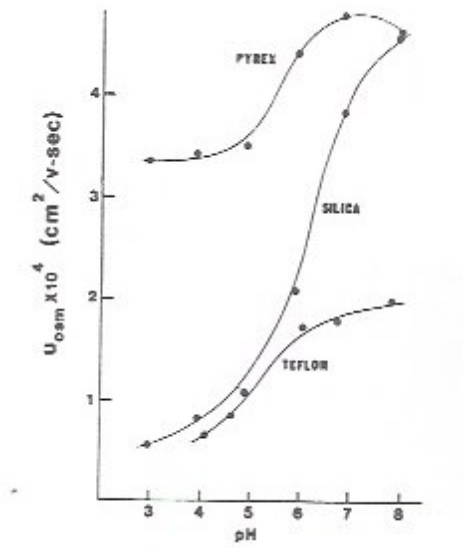


Figure 2-8: Influence of buffer pH (at constant ionic strength) on electro-osmotic flow in Pyrex glass (75µm i.d.), fused silica (75µm i.d.) and Teflon (120µm i.d.) capillaries (length 50 cm)[32].

2.1.4.2 **Electro-osmotic flow suppressors**

In order to suppress the electro-osmotic flow during the isotachophoretic analysis, a number of different reagents may be added. The most popular EOF suppressors used in the evaluated methods are (shown in Figure 2-9): hydroxyethylcellulose (HEC), hydroxypropylcellulose (HPC), Triton X-100, hydroxypropyl methylcellulose (HPMC) or Mowiol (polyvinyl alcohol).

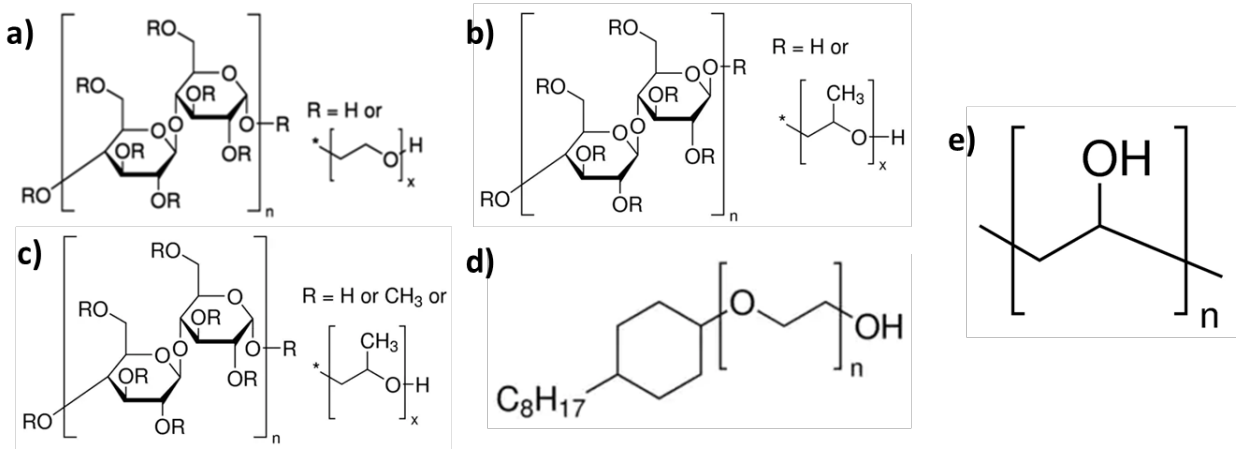


Figure 2-9: Structures of EOF-suppressing additives used in the methods. a) hydroxyethyl cellulose (HEC), b) hydroxypropyl cellulose (HPC), c) hydroxypropyl methylcellulose (HPMC), d) Triton X-100, e) Mowiol (polyvinyl alcohol).

An ideal capillary coating should be reversible and stable under the conditions required during the separation, and over a range of buffer pH. There are three basic types of capillary wall coatings: dynamic, static and hybrid coating (which is a combination of first two). Dynamic coating involves adsorptive secondary interactions, whereas static coating is based on covalent bonding between the capillary wall and the coating agent. Hybrid coating is formed from one layer held by covalent bonding while another layer is adsorbed to the adjoining surface[33,34]. Poly(vinyl alcohol) (PVA) binds more strongly to the silica surfaces than does HEC, so the columns coated with PVA have better stability.

2.1.4.3 **Complexing agents**

The analysis of ions with similar ionic mobilities may require the adjustment of the effective mobility of the ions. Examples of such complexing agents are: cyclodextrins (CD) and crown ethers (especially for group I cations). Cryptands are another class of complexing agents which are frequently reported in the literature and helpful in the analysis of the ammonium ion, lanthanoid ions, alkali metal ions and alkaline earth metal ions. Cryptands are more expensive and difficult to prepare but offer much better selectivity and strength of binding than other complexants (such as crown ethers)[35]. Figure 2-10 illustrates the typical structures for crown ethers, cryptands and cyclodextrins.

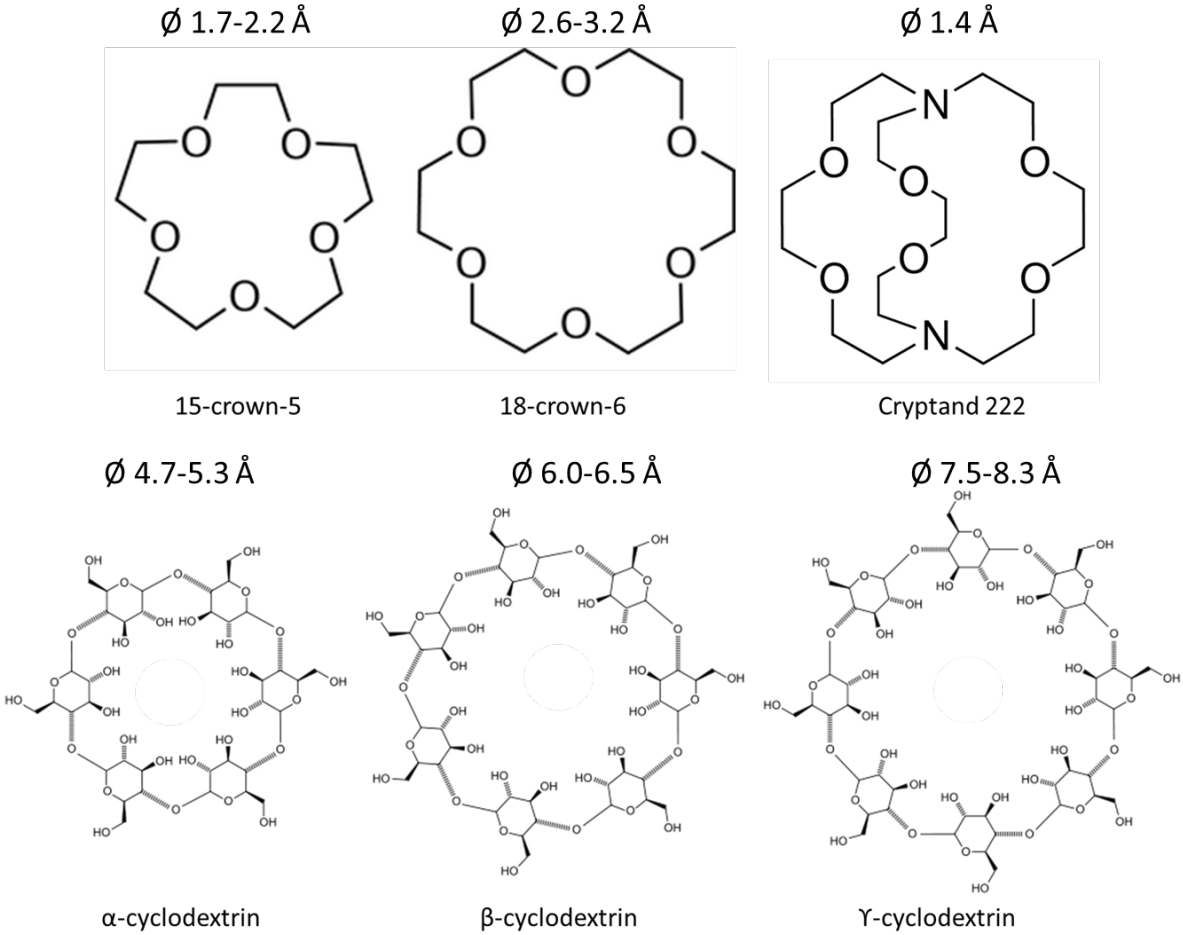


Figure 2-10: Examples of the most common complexing agents used in ITP analysis[36–40].

For the analysis of ions with similar mobilities but different atomic radii, using a complexing agent may allow separation and possible identification. Crown ether molecules can complex with metal ions by forming ion-dipole bonds with them (Figure 2-11). Cyclodextrins form sandwich-type complexes with metal ions using hydrogen bonds.

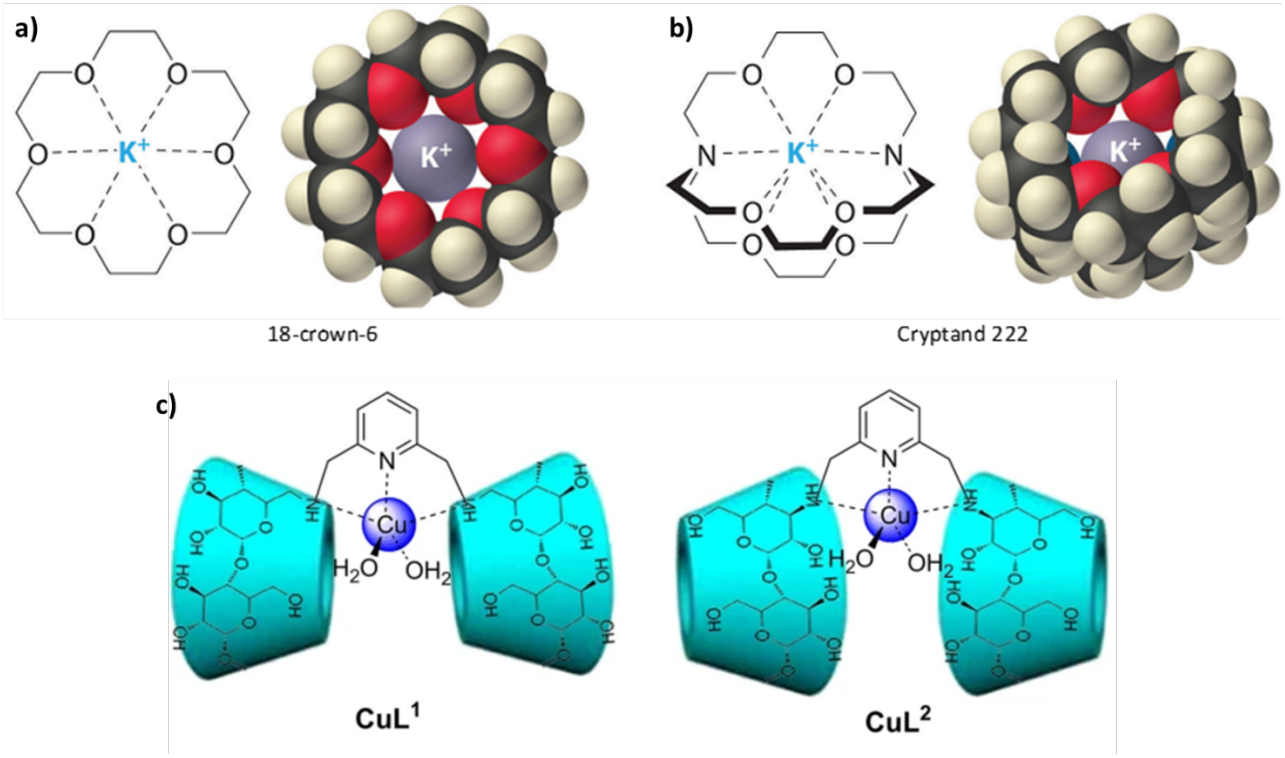


Figure 2-11: Formation of a host-guest complex between a potassium ion and a) 18-crown-6-ether[41], b) Cryptand 222[42] and c) sandwich-type metal complex with cyclodextrin[43].

2.1.5 Influence of the pH of the leading electrolyte on the ions analysed

By analysis of Figure 2-12, it can be seen that the pH has a significant effect on the species present in the solution. For the aluminium, Al^{3+} ion is present at pH below 3 and above pH 4 is in the insoluble form, $Al(OH)_3$. At pH 3, there is an equal amount of Al^{3+} ion and $Al(OH)_3$.

In ammonia analysis, below pH 6 there is only the ammonium ion present, at pH 9 there is an equal amount of NH_4^+ ion and ammonia and at pH>9 the concentration of ammonium ion decreases and ammonia increases.

The lead ion is only present at pH below 5. At pH>5 the insoluble form ($Pb(OH)_2$) dominates.

The chromium (III) ion is always present with other chromium species and above pH 6, it is only present as insoluble Cr_2O_3.

The iron (II) ion is present at pH below 6. Above pH 6 the other species is present in form of insoluble $Fe(OH)_2$.

In copper analysis below pH 6 there is only copper II ion present, at pH 6.5 there is an equal concentration of Cu^{2+} ion and CuO, at pH>6.5 there is only insoluble oxide present.

The calcium ion is present in the solution at pH below 10, at pH>10 there is a mixture of calcium ion and $CaOH^+$.

The magnesium ion is present at pH below 9. Above pH 9 there is only insoluble magnesium hydroxide present.

Many electrolytes need adjustments of the pH before the experiment. That requires careful selection of the pH of the leading electrolyte, depending upon the species present in the sample solution. Some of the ions are not affected by pH changes (such as: Cu^{2+}, Mg^{2+} and Ca^{2+}), where the ion form is present in the solution in wide range of pH.

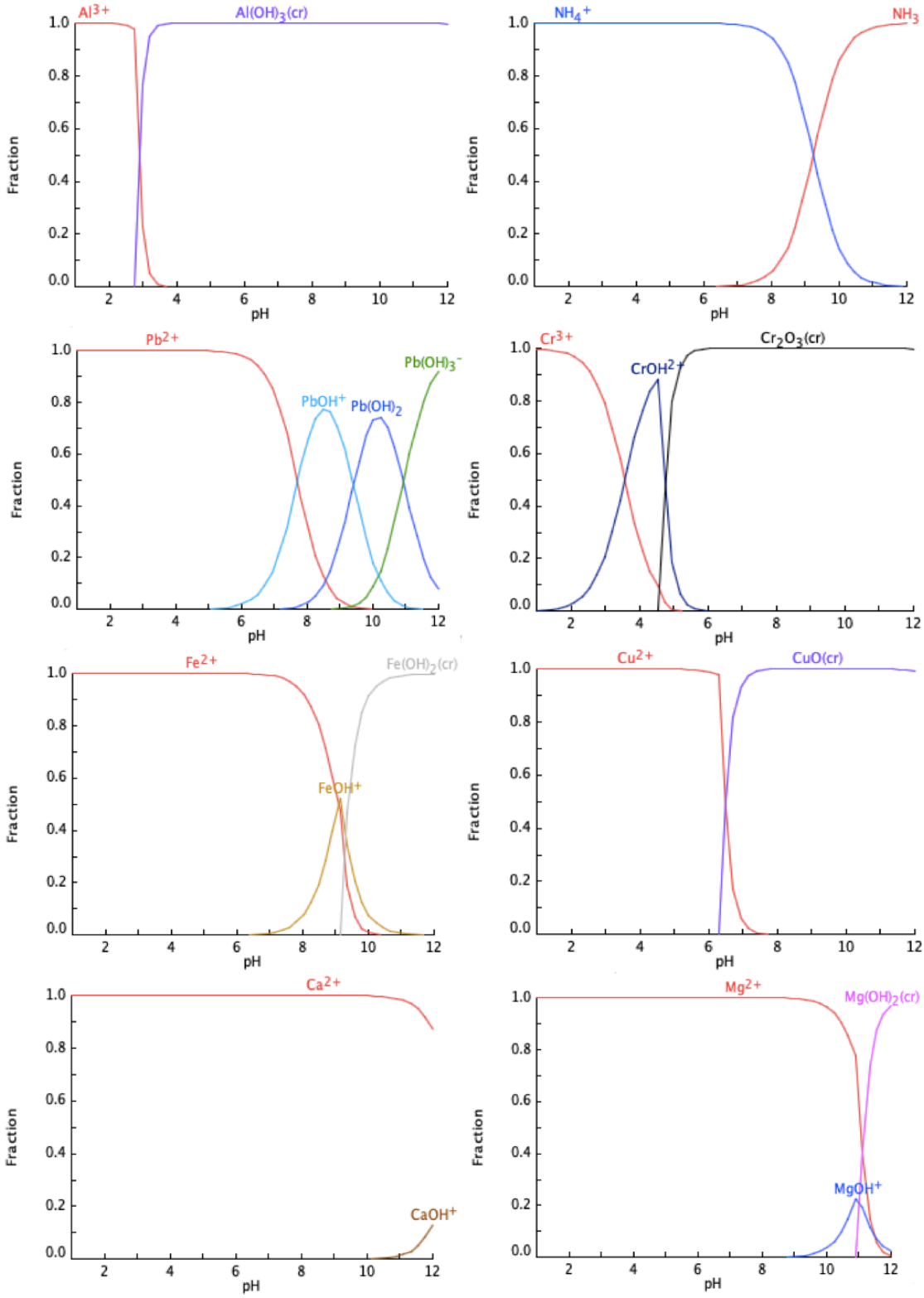


Figure 2-12: Graphs showing the influence of pH on the ionic species present in the aqueous sample (fraction vs pH) for: aluminium, ammonium ion, lead, chromium, iron, copper, calcium and magnesium. Graphs prepared by Hydra-Medusa software.

2.1.5.1 Examples of the influence of pH of the LE on the samples

The influence of the pH of the leading electrolyte was investigated further. Analysis was done to explore the possibility of analysis of samples with lower concentrations (where steps were longer). The analysis of the relative step height within the separation may be important in the analysis of mixtures where more than one component has the same or similar RSHs and thus will not be separated and give incorrect results (steps would overlap). Slightly changing the pH may promote the separation.

Figure 2-13 presents examples of the influence of the pH of the leading electrolyte on the RSH and step length. It may be seen that only in one case, chromium (III) ion analysis, there is a trend in the RSH and step length. The higher the pH, the higher the RSH but shorter the step. However, the difference in step length is not significantly changed.

The same electrolyte system was used in the experiments with iron (II) ions and there is no trend at all in either RSH or step length data. However, LE at pH 4.9 which was used in all calibrations and analysis gives the longest step and the lowest step height.

In the analysis of copper (II) ion it may be seen that the pH of the leading electrolyte does not influence of RSH or step length. While in the lead ion experiments, the influence of pH of leading electrolyte dose not have much influence on the separation.

All systems provide separation of ions using a leading electrolyte with acidic pH between 4 and 6, only copper (II) ion gives satisfying results at higher pH 7 and 8. All samples were analysed at pH 3 however it did give inconclusive results. Chromium (III), iron (II) were also analysed at pH 6 however no steps were detected. Lead (II) ion was examined at pH 7 and 8 but there was no steps (ion) present.

A change of pH of the leading electrolyte has a great potential in mixed sample separation. Unfortunately, there is no compiled library reference data in journal literature available for researchers to help to decide which pH would be the most appropriate in the particular analysis. This project shows only that there is a difference in the steps lengths and RSHs which could be a valuable reference source if developed and investigated further.

The pH of the electrolytes was measured using a Mettler Toledo FiveEasy plus - pH meter. The pH meter was calibrated before every measurement using two pH buffers (pH 4.01 and 7.0).

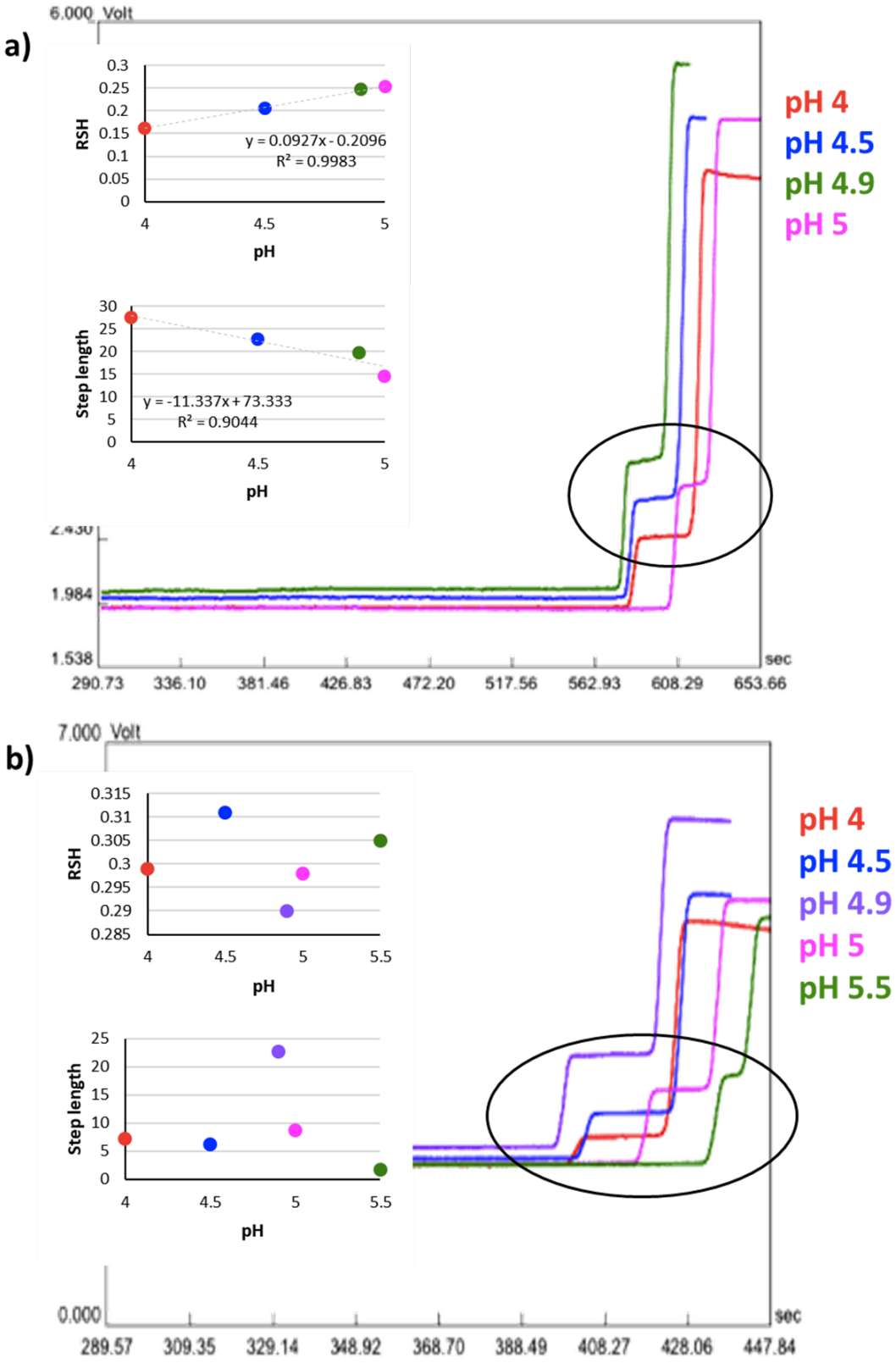


Figure 2-13: Analysis of some samples using leading electrolytes with different pH. a) 30 mg/l of Cr^{3+}, b) 30 mg/l of Fe^{2+} using electrolyte system consisting of LE: 10mM NaOH, 2.5mM malic acid, 1 mg/ml HEC, pH adjusted by propionic acid; TE: 10mM TBA.

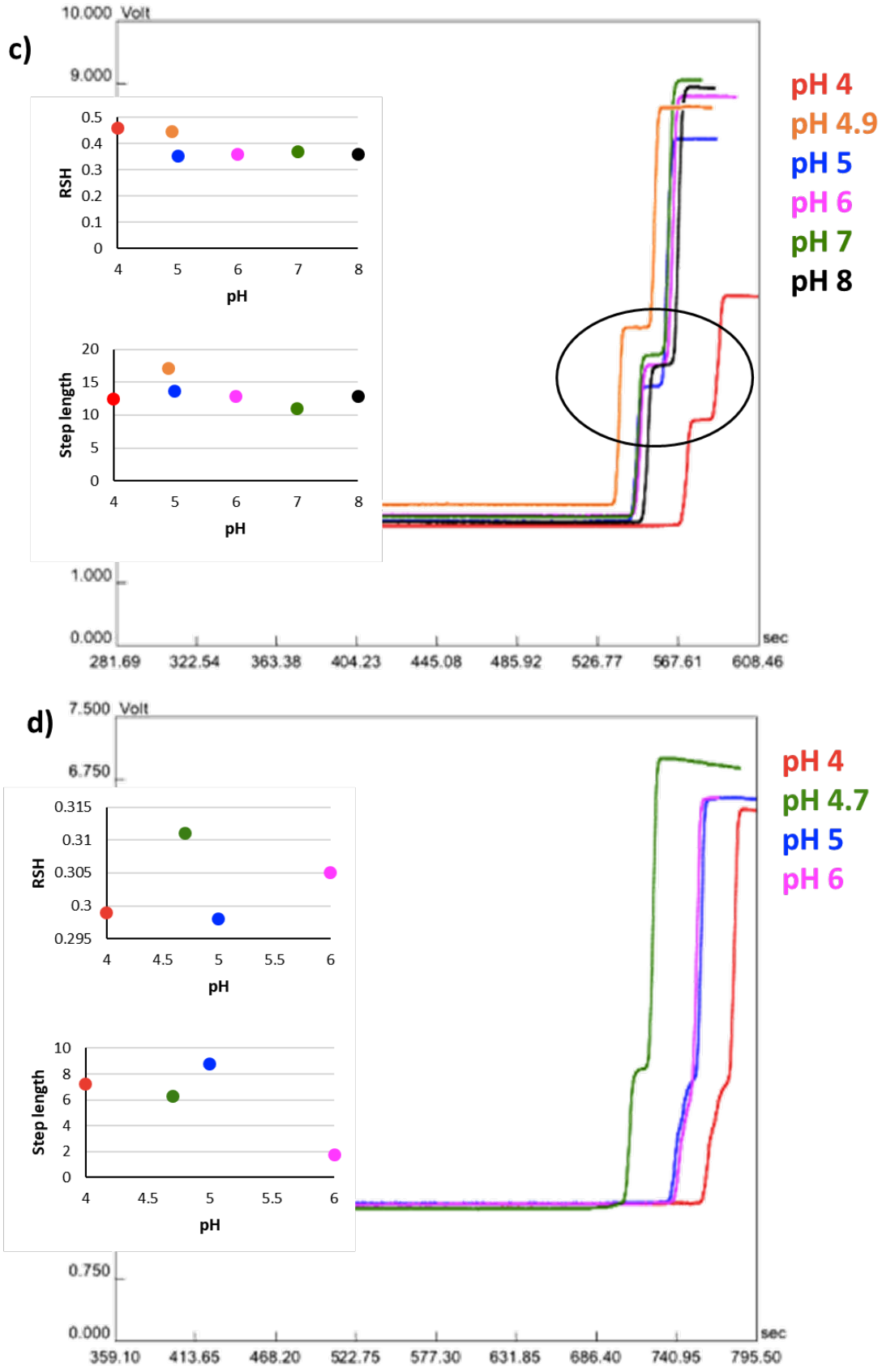


Figure 2-13: Analysis of some samples using leading electrolytes with different pH. c) 20 mg/l of Cu^{2+}, LE: 10mM NaOH, 5mM HIBA, 0.1% HEC, pH adjusted by propionic acid; TE: 10mM Car Hydro; d) 30 mg/l of Pb^{2+}, LE: 10mM CsOH, pH adjusted by HAc; TE: 10mM TBA.

2.1.6 **Applications of ITP**

Isotachophoresis is used in the separation of anions and cations, organic and amino acids, peptides, nucleotides, nucleosides and proteins. The main industries which are using ITP are chemistry, biochemistry, food, environmental and pharmaceutical chemistry. Chapter 13 presents lists of the isotachophoretic systems used to separate various samples. The number of methods shows how versatile and powerful the technique is. In majority of the cases, if the sample is prepared in aqueous solution, the sample preparation is not required.

2.1.7 **ITP Instrumentation**

The ItaChrom II EA 202M instrument (Figure 2-14 and Figure 2-15) was used in the project.

The main components of the isotachophoresis instrument are:

- Separation unit containing a coupled column
- Power supply – high voltage with high-voltage relay (column-switching)
- One contactless conductivity detector on each column (pre-separation and analytical columns)
- Detector – on-column UV absorbance photometric detector on the analytical column
- Control unit and computer

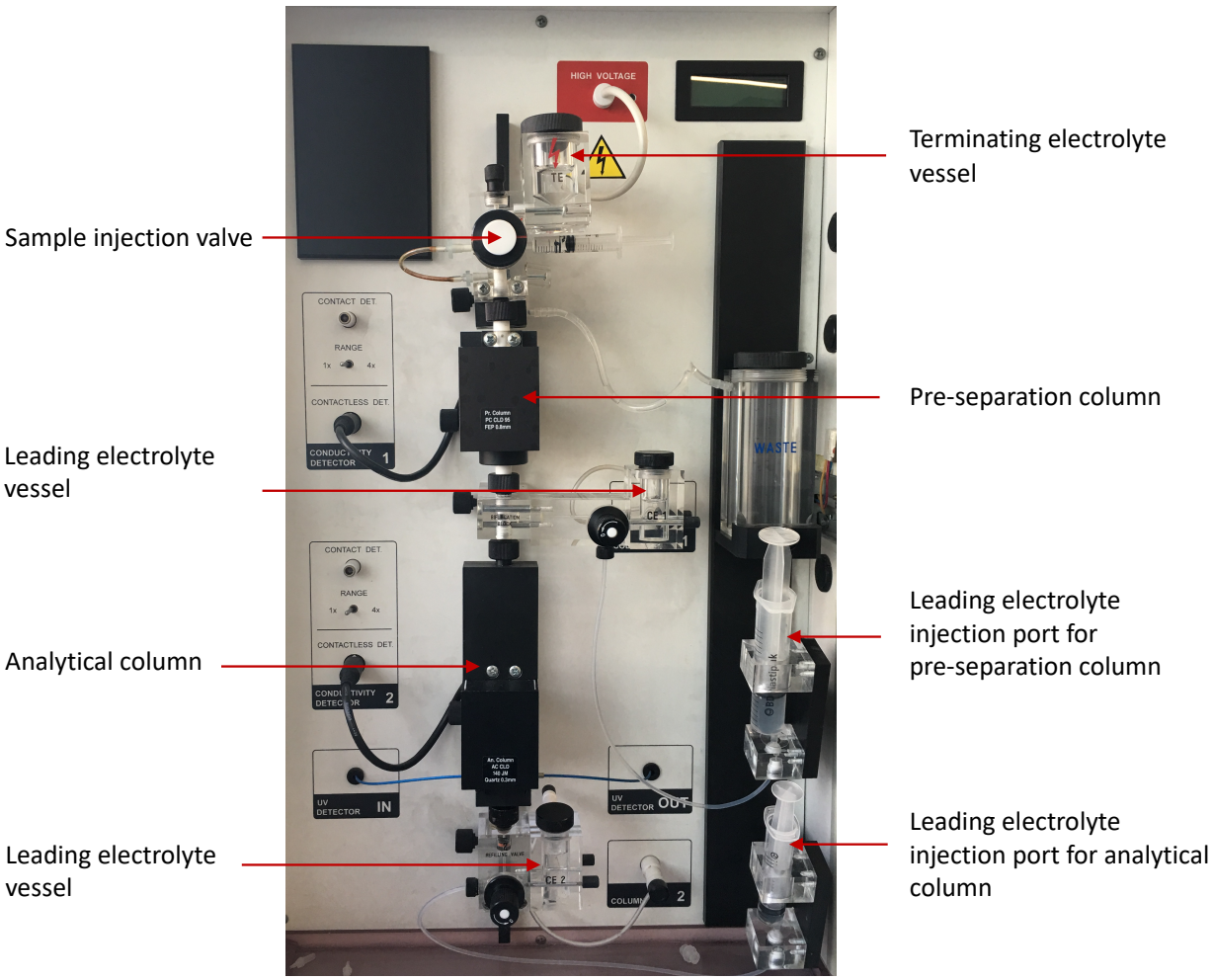


Figure 2-14: The Isotachophoresis Instrument ItaChrom II EA 202M.

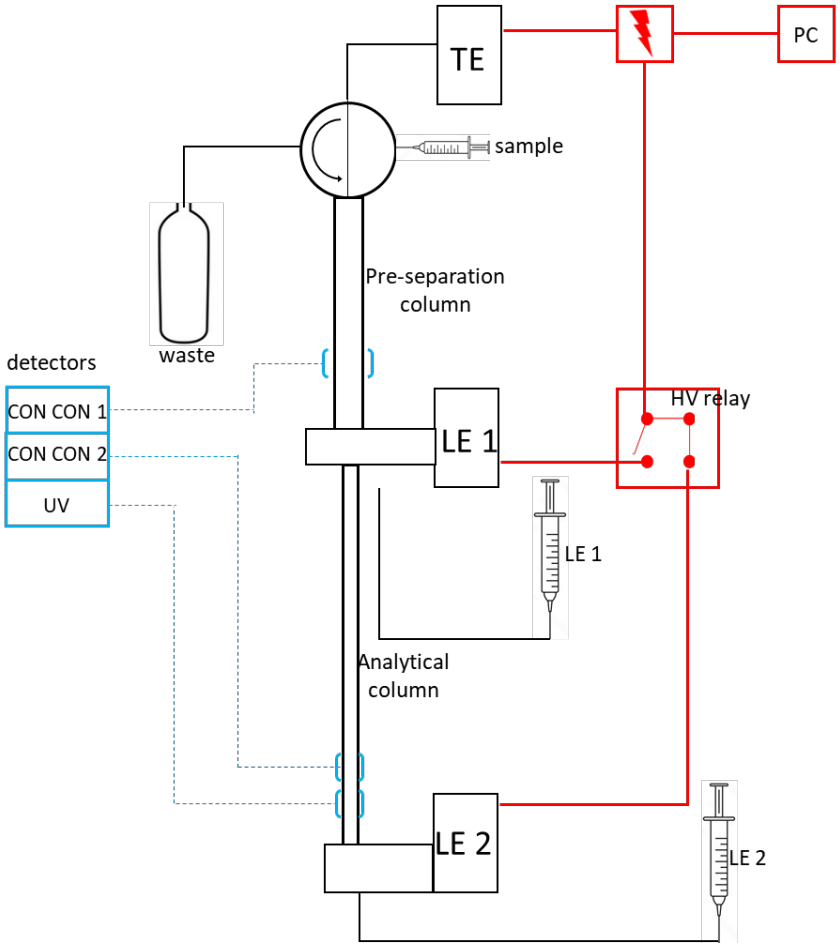


Figure 2-15: **:** Schematic diagram of the isotachophoresis instrument ItaChrom II EA 202M, where *CD1* and *CD2* are contactless conductivity detectors of the columns (pre-separation and analytical columns), *HV POWER SUPPLY* is high voltage power supply, *UV* is UV absorbance photometric detector of the analytical column, *CONTROL UNIT* is system controller, *PC* is computer and *HIGH-VOLTAGE RELAY* is high-voltage (column-switching) relay[44].

2.1.8 **Instrument programs used during the experiments**

Table 2-3 presents separation conditions used during ITP analysis, the methods varied in times and current used. All separation were performed in the upper (pre-separation) column.

Table 2-3: Instrument timing and current programs used during the experiments. a) presents 'lead method'; b) shows 'method 3'; c) 'ammonium method' and d) 'cs ac method'.

a)

Step	Time	Current	Comp	Column	Cond	UV
1	250	150	0	Upper		
2	1000	100	0	Upper	X	

b)

Step	Time	Current	Comp	Column	Cond	UV
1	250	500	0	Upper		
2	1000	400	0	Upper	X	

c)

Step	Time	Current	Comp	Column	Cond	UV
1	200	300	0	Upper		
2	1000	150	0	Upper	X	

d)

Step	Time	Current	Comp	Column	Cond	UV
1	250	350	0	Upper		
2	300	200	0	Upper	X	

2.1.9 **Separation methods used in the project**

During the project many methods were researched for various ions. These are covered in Chapter 13. Table 2-4 documents the ones that were the most suitable and used in the project. The electrolyte number system does not correspond to the table in the appendix. It has been used since the start of the project and remained for the consistency.

Table 2-4: Electrolyte system used in ITP separations (for abbreviations please see page 15).

Electrolyte system	**4**	**5**	**12**	**13**
LE	10mM NaOH	10mM NaOH	30mM NaOH	20mM NaOH
Complexing agent	5mM HIBA	2.5mM malic acid	15mM HIBA	—
pH buffer	Propionic acid	Propionic acid	Propionic acid	HIBA to pH 5.0
pH	4.9	4.9	4.9	HAc to pH 4.1
Additive	0.1% HEC	0.1% HEC	0.1% HEC	—
TE	10mM Car Hydro	10mM TBA	10mM Car Hydro	5mM HCl
Analysed ions	Cu,Cr(III),Pb	Cr(III),Fe(II)	Cu	Al

Electrolyte system	**21**	**26**	**48**	**57**	**85**
LE	10mM CsOH	20mM NH_4OH	10mM HCl	10mM HCl	10mM CsOH
Complexing agent	—	10mM HIBA	—	—	—
pH buffer	His	HAc	—	—	HAc
pH	9.0	4.8	—	—	4.7
Additive	—	0.2% HPC	0.05% mowiol	—	—
TE	10mM lithium citrate	10mM Car Hydro	10mM Tris	10mM Tris	10mM TBA
Analysed ions	Ca,Mg,NH_4^+	Ca,Mg,Cu,Pb	Ca,Mg,Cu,Pb,Al, Cr(III),Fe(II), NH_4^+	NH_4^+	Pb

2.1.10 **Detector used during the experiments**

The detector used during the experiments was a contactless conductivity detector. The instrument used has two contactless detectors, one on each column. The detector measures the potential of the electrolyte while a small constant current is passing through. Ions are detected by the difference in conductivity to the background electrolyte. Usually, the conductivity of the separated zones is defined by both the zone concentration (which usually matches the concentration of the primary

ion in the LE) and the ionic mobility of the separated ion in a given zone. The main advantage of the contactless detector is that the sample does not come in to contact with the electrodes, so the sample is not affected by the imposed current.

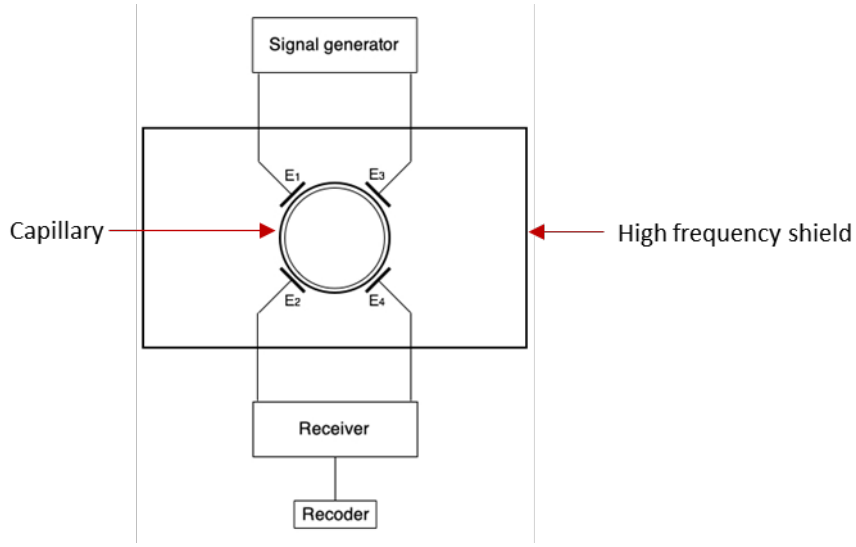


Figure 2-16: Schematic diagram of the contactless detector used in ITP analysis.

The contactless conductivity detector consists of the four copper electrodes (E_1, E_2, E_3 and E_4 in Figure 2-16) on the outside wall of the capillary. The generator produces a high frequency signal which is imposed by the emitting electrodes E_1 and E_3 to the sample. Then electrodes E_2 and E_4 receive the signal and the receiver translates the signal into data which is visible at the recorder as series of steps[45,46].

2.1.11 **Calibration of the conductivity detector**

The detector was calibrated by using different concentrations of a potassium chloride (KCl) standard solution. Columns and all vessels were filled with the same electrolyte and then current passed through. After the voltage was stable it was noted down and used to calculate the conductance of the particular concentration of KCl at a particular current.

According to Ohm's Law the voltage (*V*) set up across the solution is proportional to the current (*I*) as shown in Eq 5.

The resistance (*R*) is a constant of proportionality and can be calculated with the measured current if a known voltage is applied:

$$V = R \cdot I \Rightarrow R = \frac{V}{I} \left[\frac{V}{A}\right] \qquad \text{(Eq 5)}$$

Where *V* is voltage [V], *R* is resistance [Ω] and *I* is current [A].

Conductance (*G*) is defined as the inverse of resistance:

$$G = \frac{1}{R} \qquad \text{(Eq 6)}$$

Where *G* is conductance [Siemens].

Eq 6 is made from Eq 4 and Eq 5. It was used in calculation of conductance of calibration solutions as shown in Table 2-5.

$$G = \frac{1}{\frac{V}{I}} = \frac{I}{V}\ [S] \qquad \text{(Eq 7)}$$

Molar conductance (Λ) in chemical solutions is calculated as follows:

$$\Lambda = \frac{\kappa}{C}\left[\frac{S}{m} \cdot \frac{m^3}{mol} = \frac{S \cdot m^2}{mol}\right] \qquad \text{(Eq 8)}$$

Where $\kappa\left[\frac{S}{m}\right]$ is specific conductance and $C\left[\frac{mol}{m^3}\right]$ is concentration.

Table 2-5: Results of the analysis of different concentrations of KCl using different applied constant current.

	Concentration [M]											
	0.1M		**0.05M**		**0.01M**		**0.005M**		**0.001M**		**0.0005M**	
Current	**V**	**G**	**V**	**G**	**V**	**G**	**V**	**G**	**V**	**G**	**V**	**G**
100 µA	83	1.205	103	0.9709	298	0.3356	488	0.2049	2100	0.04762	3473	0.02879
200 µA	112	1.786	161	1.242	547	0.3656	923	0.2167	3614	0.05534	5739	0.03485
300 µA	147	2.041	215	1.395	772	0.3886	1314	0.2283	4781	0.06275	7341	0.04087
400 µA	181	2.210	269	1.487	982	0.4073	1612	0.2481	5602	0.0714	8532	0.04688
500 µA	215	2.326	322	1.553	1162	0.4303	1856	0.2694	6442	0.07762	9368	0.05337

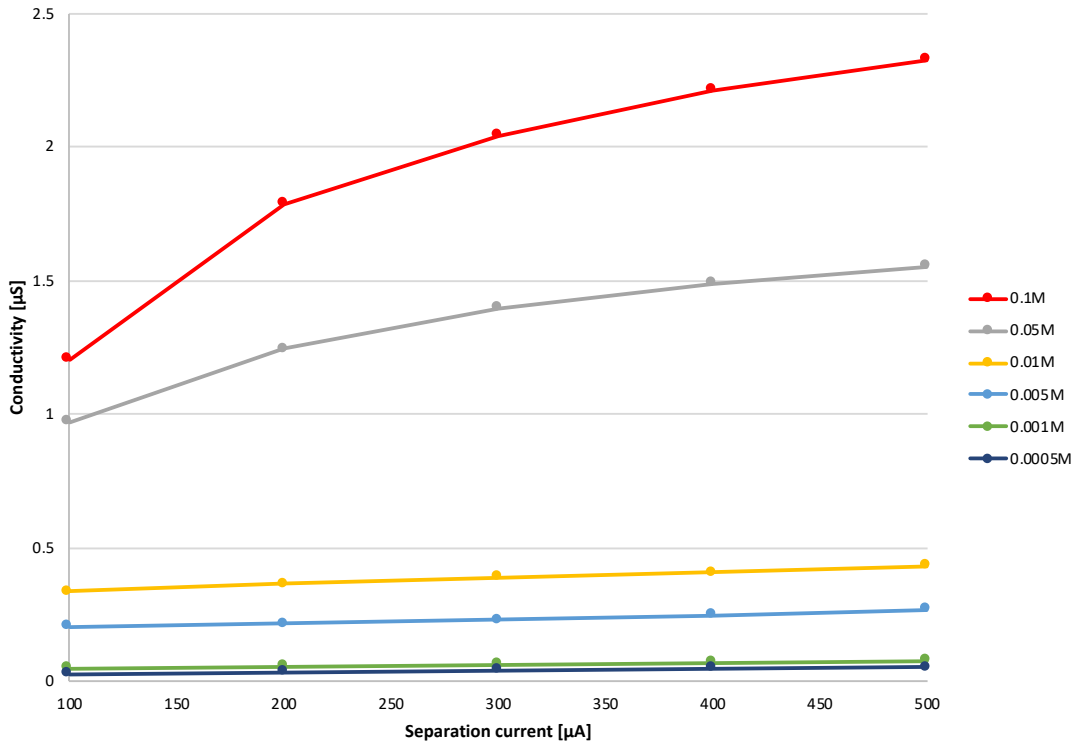


Figure 2-17: Calibration graph for detector calibration (conductivity vs current). Points are connected by straight lines to guide the eye.

Analysing Figure 2-17 it is possible to notice that lower concentrations (below 0.01M) give a linear response while higher concentrations do not. That proves that ITP gives better results analysing low concentrations (≤0.01M) so in analysis of concentrated samples, dilution may be required. That would also reduce separation time (the step length would decrease). The detector is only measuring conductivity using four electrodes, so the separation current should not affect the conductivity (as seen for 0.01M, 0.005M, 0.001M and 0.0005M KCl). For higher concentrations there is much greater difference in conductivity, that may be due to the effect of the increasing temperature of the system.

The prototype detector was calibrated in the same way and the results are discussed in Section 8.5.3.

2.1.12 **Joule Heating**

In isotachophoretic analysis, like in every electrophoretic technique, the temperature rises during the process due to Joule heating. The interaction between applied electric field and ionic components in the sample is responsible for the Joule heating. The amount of generated heat depends on the electric field and the conductivity of buffer. During the ITP analysis, the conductivity, electric field and buffers vary, hence the amount of heat is not constant throughout the system[47]. Joule heating may be calculated using the following equation:

$$W = I^2 \cdot R = \frac{I^2}{G} \qquad \text{(Eq 9)}$$

Where *I* is current [A], *R* is resistance [Ω], *W* is power in Watts (Joule heating) and *G* is conductance [S].

Joule heating may result in viscosity or density changes of the solvents, pH variation in the system, degradation of the analytes, denaturation of the protein samples or even partially evaporation of the samples. That may result in inaccurate results and decreased concentration of the analyte. Figure 2-18 presents isotachopherograms showing how Joule heating is identified in the ITP analysis.

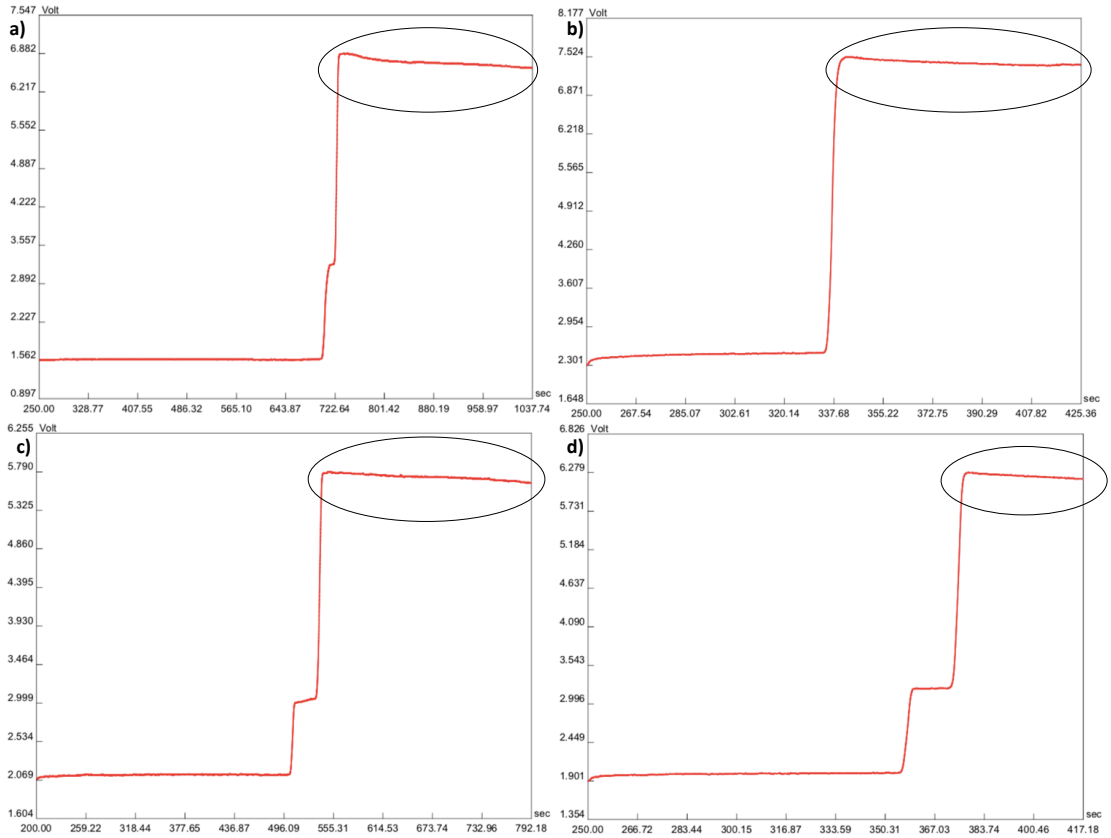


Figure 2-18: Effect of Joule heating during the ITP analysis (marked in the ellipse).
a) 40 mg/l of Pb (II), LE: 10mM CsOH, pH 4.7 by acetic acid, TE: 10mM TBA ('lead method'); b) Blank sample, LE: 10mM NaOH, 2.5mM malic acid, 0.1% HEC pH 4.9 by propionic acid, TE: 10mM TBA ('cs ac method');
c) 40 mg/l of Cr (III), LE: 10mM NaOH, 2.5mM malic acid, 0.1% HEC pH 4.9 by propionic acid, TE: 10mM TBA ('ammonium method');
d) LE: 10mM NaOH, 2.5mM malic acid, 0.1% HEC pH 4.9 by propionic acid, TE: 10mM TBA ('cs ac method').
Electrolyte system used in a) was 85 and for b), c) and d) was 5.

Chapter 3 Ion chromatography (IC)

Ion chromatography separates components based on their ionic interactions with and partitioning between mobile (H^+) and stationary phases ($\ominus$) as seen in Figure 3-1[48]. In cation analysis, cations equilibrate between the mobile and the stationary phase such that cations with a stronger affinity for stationary phase will take longer to transit the column and will therefore be retained longer.

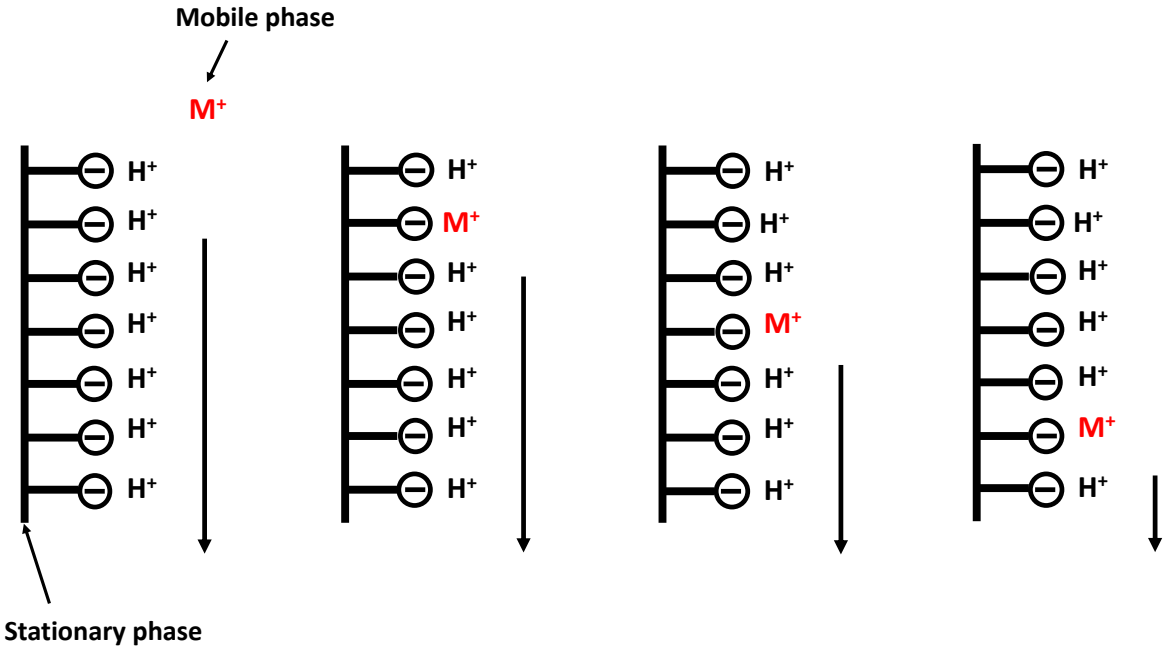


Figure 3-1: Schematic of the principle of the ion chromatography for cationic separations. M^+ represents an ion and arrow shows the direction of flow of the mobile phase.

Figure 3-1 shows how the sample transits during the separation time. First figure on the left hand side presents the system at the injection time, then how the ion sample travels through the column and last figure presents the separation towards the end. The sample is carried by an eluent (mobile phase), the different ions are separated in a column packed with an ion exchange resin (stationary phase). In analysis of cations, the active resin will have a negative charge. Individual ions attach and detach from the resin. Ions with greater affinity for the stationary phase are retained in the column for longer. Ion chromatography is widely used in many industries, including: waste water analysis, food and cosmetics, isolation of proteins and pharmaceuticals.

3.1.1 **Instrument**

The ion chromatography instrument used in the project was a Thermo Scientific ISC Dionex 5000+. The most important components of the instrument are the guard and separation columns, eluent generator, suppressor, pump and autosampler.

Figure 3-2: Ion chromatography instrument Thermo Scientific ICS 5000.

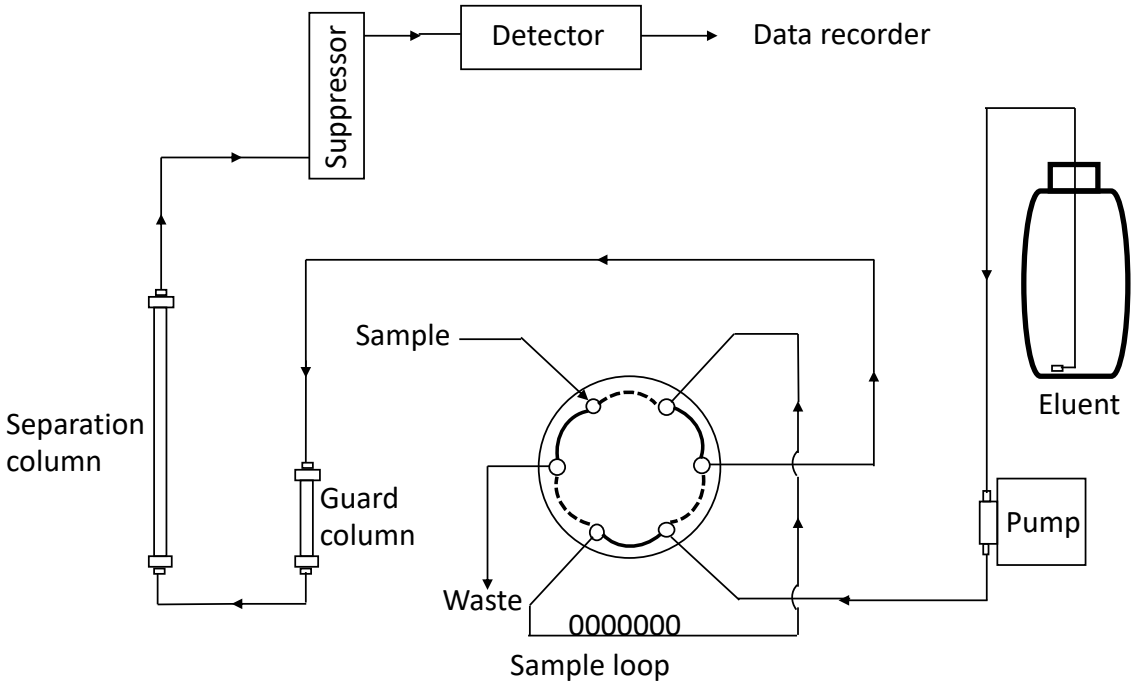


Figure 3-3: IC instrument (ThermoFisher Scientific Dionex 5000+).

3.1.2 **Columns used in the project**

The separation column used was a Dionex IonPac CS12A (2x250mm), this particular column was designed for the analysis of ammonium and other common cations in drinking, process and industrial waters. The guard column is used to capture all bigger particles so the analytical column will not get blocked.

3.1.3 **Instrument method used in the project**

Samples were delivered by an autosampler in equal volumes of 25µl. Samples were stored in the 1.5ml polypropylene vials with white silicone/blue PTFE septa. All the experiments conducted during this project, used a mobile phase of 20mM of methanesulfonic acid. The flow rate of the mobile phase was 0.25 ml/min.

3.1.4 **Eluent generator**

The eluent generator provides a continuous supply of the mobile phase and consists of the stock solution and ultra-pure water. The final eluent concentration may be programmed using the software.

3.1.5 **Suppressor**

The suppressor plays a key part in the ion chromatography analysis. After separation, the suppressor reduces the conductivity of the eluent by exchanging the eluent and sample counter ions with suppressor derived ions. It reduces the background conductivity and also enhances the conductivity of the analytes. Thus, it helps to increase detector sensitivity and minimises background noise.

3.1.6 **Detector used in ion chromatography**

Ion chromatography uses a universal conductivity detector which measures conductance of the eluent. It gives high sensitivity and specificity, robustness and high reproducibility. It measures the solution resistance between two electrodes within the flow cell.

3.1.7 **Data analysis**[49,50]

The results of the chromatographic analysis are presented as a chromatogram and are expressed as series of peaks (Figure 3-4). Each peak corresponds to a different sample component (ion). The first negative peak in the Figure 3-4 represents the injection of the sample and is result of the sample solvent used. Thus, that peak could be either negative or positive depending on the mobile phase and sample solvent used. Most of the time this peak does not appear in the chromatogram. Standard analyses provide information about the retention time for each analyte which is characteristic to the species in the given system and allows peak identification in the sample mix. The peak height or peak area is used in preparation of calibration graphs.

Retention time (t_R) is the time needed for a compound to move from the injection point to the detector. This time is composed of two components, dead time and solute retention time (Eq 10). Dead time (t_M) is the time required for a nonretained compound to pass through the column. It is the same for all chromatographic separations in the particular system. Solute retention time (t_s) is the time the solute spends retained by the stationary phase.

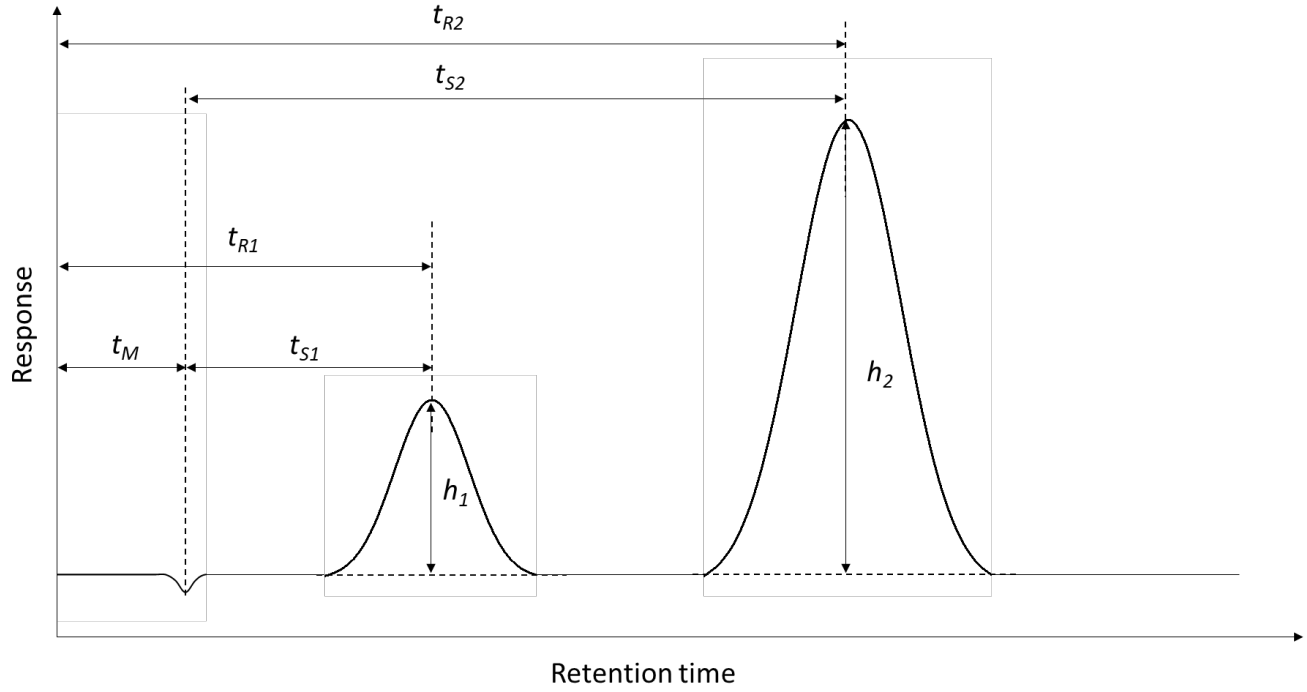


Figure 3-4: Example of the chromatogram showing data points used in the calculation of retention times.

The gross retention time (t_R) is calculated as follows:

$$t_R = t_M + t_S \qquad \text{(Eq 10)}$$

There are two possible ways to quantify the chromatogram, it is either by peak height or peak area. The only condition is that the column does not get overloaded, there is a simple method to check that. Calculate the ratio of peak height and peak area, that should give a constant value.
The calibration graph for each analyte plots the concentration against the peak height.

3.1.8 **Peak shape**[51]

Generally, all peaks in chromatograms are Gaussian curves where the width of the peak (ω) at the baseline is four times the standard deviation (σ) of the curve. In the perfect peak, the baseline peak width is two times greater than the peak width at half of the peak height ($\omega_{1/2}$).

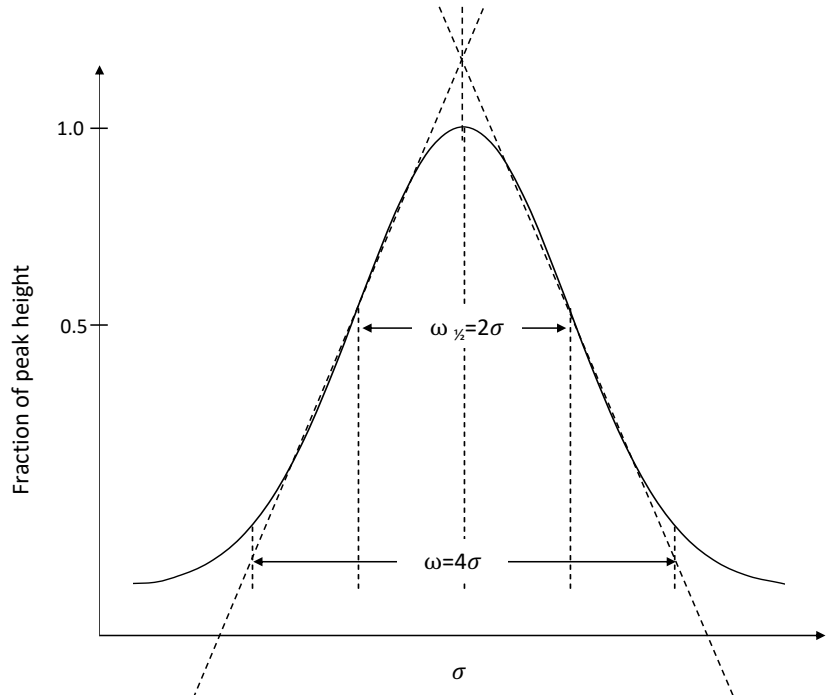


Figure 3-5: Idealised Gaussian peak (representative of an ideal chromatographic peak), σ is standard deviation and ω is peak width.

3.1.8.1 **Asymmetry factor**[52]

The majority of the peaks are asymmetrical to some extent. Peaks in chromatographic analyses are considered as practically Gaussian when the asymmetry factor (A_s) is between 0.9 and 1.2. A mathematical formula used to calculate that factor is based on Figure 3-6 and is represented by the following equation:

For c = 0.1

$$A_s = \frac{b}{a} \qquad \text{(Eq 11)}$$

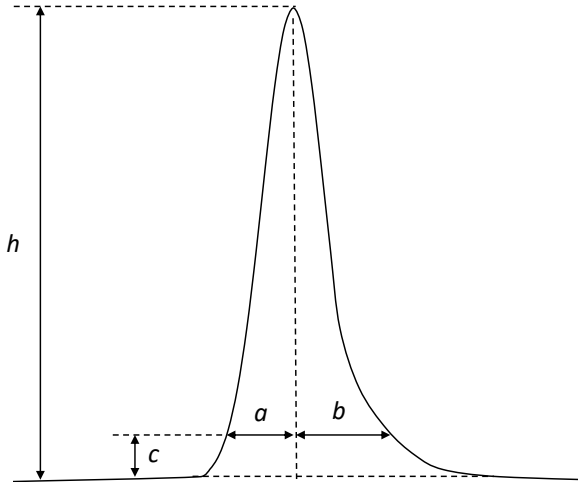


Figure 3-6: An example of an asymmetric peak.

3.1.9 **Resolution of peaks**[49]

Efficient chromatography analysis allows both quantitative and qualitative information. The correct identification is only possible if all peaks are well resolved. Resolution (*R*) of two adjacent peaks is defined as the difference of the two peaks retention times (Δt) and the arithmetic mean of the respective peaks' widths (ω) at the peaks' base (Eq 12). If the *R*=1.5 peaks are sufficiently resolved for quantitative analysis. Thus, peaks are completely resolved.

$$R = \frac{t_{r1} - t_{r2}}{\frac{\omega_1 + \omega_2}{2}} = \frac{2\Delta t}{\omega_1 + \omega_2} \qquad \text{(Eq 12)}$$

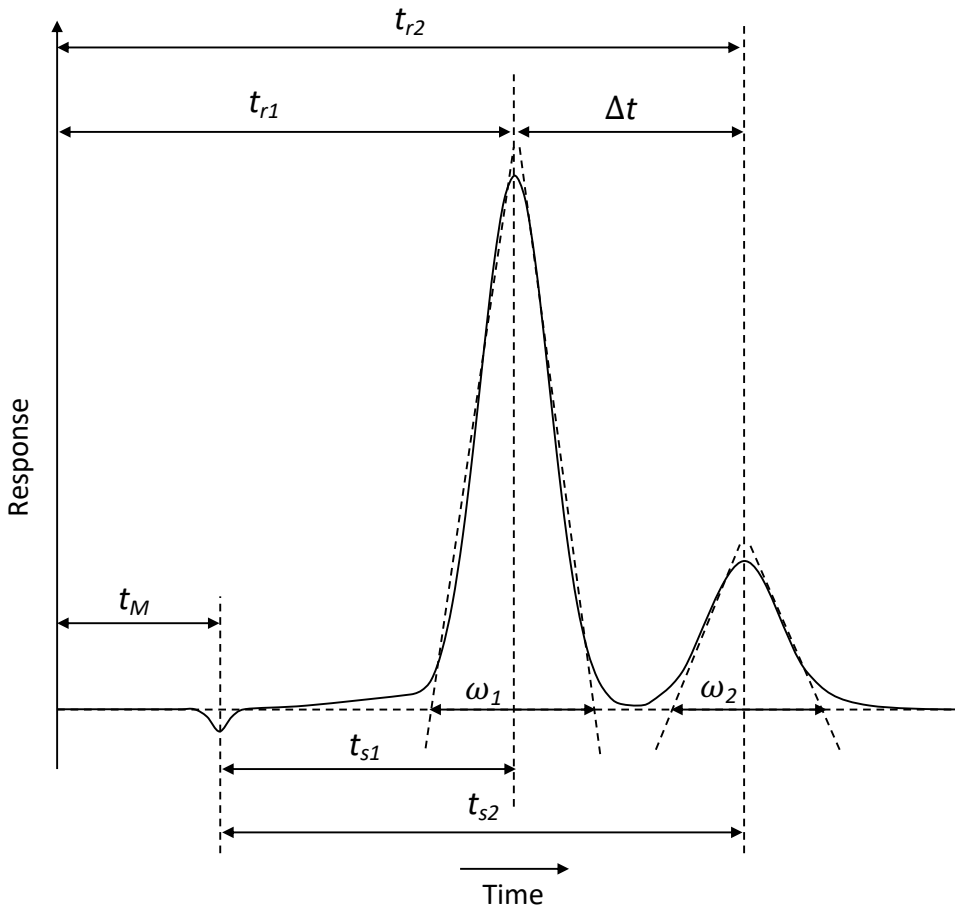


Figure 3-7: An example of the data available from the peaks of a chromatogram for the determination of resolution, selectivity and capacity factors.

3.1.10 **Selectivity in the chromatographic analysis**

Selectivity (α) is the parameter to distinguish whether separation has occurred (Eq 13). If $\alpha = 1$ there is no difference between the peaks, so the separation has not been possible under the given separation conditions. Only if $\alpha = 0$ the two peaks are fully separated.

$$\alpha = \frac{t_{r2} - t_M}{t_{r1} - t_M} = \frac{t_{s2}}{t_{s1}} \qquad \text{(Eq 13)}$$

3.1.11 **Capacity factor**[49]

The capacity factor (*k*) is the ratio of the time spent by the solute in the stationary phase to the time spent in the mobile phase (Eq 14). Small values of capacity factor suggest that the components elute near the equivalent void volume, thus the separation is poor. However high values correspond to

longer separation times which may be followed by peaks broadening and associated decreased sensitivity.

$$k = K \cdot \frac{V_s}{V_m} = \frac{C_s \cdot V_s}{C_m \cdot V_m} = \frac{t_r - t_M}{t_M} = \frac{t_s}{t_M} \qquad \text{(Eq 14)}$$

K - Nernst distribution coefficient

V_s - volume of stationary phase

V_m - volume of mobile phase

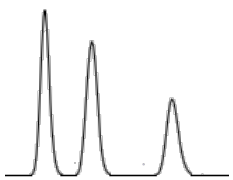
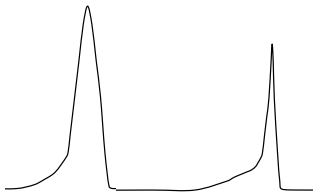
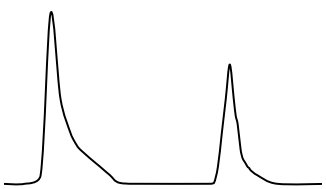
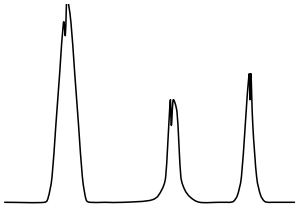
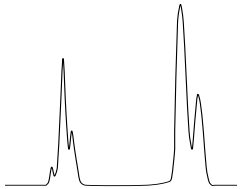
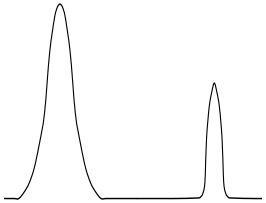
C_s – solute concentration in the stationary phase

C_p – solute concentration in the mobile phase

3.1.12 **Troubleshooting during chromatography analysis**[53]

Analysis of the chromatograms allow recognition of the sample component as well as determination of its concentration, optimisation of the separation method results in well-shaped and well-resolved peaks. However, sometimes especially during preliminary experiments, there may be some problems with the peaks' presentation. Table 3-1 presents the most common problems, their sources and possible solutions.

Table 3-1: Troubleshooting associated with chromatograms analysis.

	Problem	Normal peaks	Fronting	Tailing	Split peaks	Overlapping peaks	Broad peaks
	Example						
	Description	Sharp, well-defined, symetric and well-resolved peaks	Peak distortion occurring in front of the peak.	Peak distortion occurring in the end of the peak.	Split peaks, unable to determine a concentration	Peaks overlapping, sample components not separated	Wide peaks, much broader than usual.
1	**Possible cause**	—	Low temperature.	Sample reacting with the active sites.	Contamination of the analytical or guard column.	Temperature too high.	Mobile phase flow rate too low.
	Solution	—	Increase temperature.	Change column.	Flush the column, if problem persists change the column.	Decrease temperature.	Increase the flow rate.
2	**Possible cause**	—	Wrong sample solvent.	Interfering peak.	Sample solvent incompatible with mobile phase.	Column too short.	Column overloaded.
	Solution	—	Use mobile phase as sample solvent.	Use longer column, change mobile phase or column.	Use mobile phase as a solvent.	Use longer column.	Dilute sample or just smaller injection volume.
3	**Possible cause**	—	Sample overload.	—	—	—	Peaks represent more than one component.
	Solution	—	Dilute the sample.	—	—	—	Change column for better resolution.

Chapter 4 Inductively coupled plasma – optical emission spectrometry (ICP-OES)[54,55]

During ICP-OES analysis plasma energy (ionised gas) excites the elements to be analysed in a solution-phase sample. Once excited, the atoms return to the low energy position (ground state) which results in photon emission (Figure 4-1). The intensity is proportional to concentration and yields no qualitative information. The emission wavelength(s) are selected to be selective (and in some cases specific) for the elements for which the analysis is carried out. Wavelength and intensity of the photon flux is characteristic for an element.

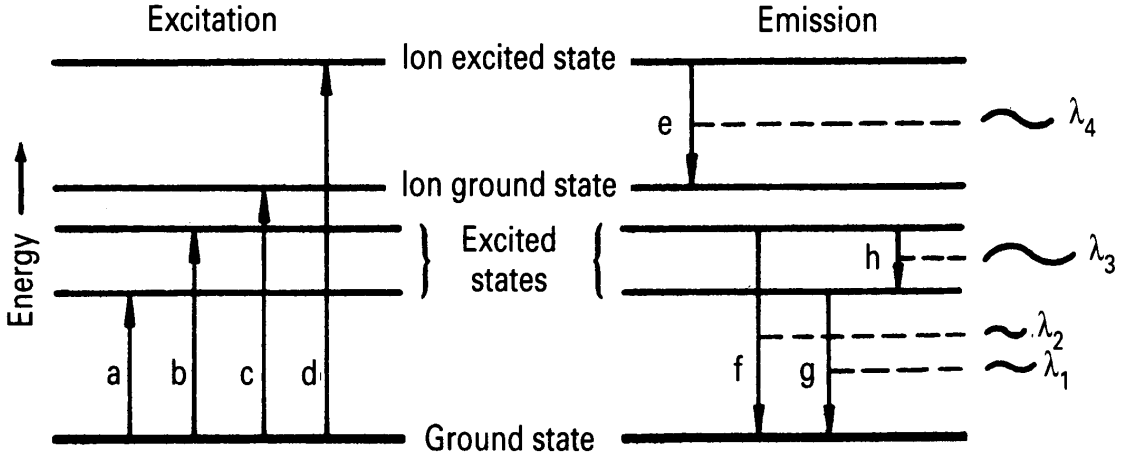


Figure 4-1: Jablonski energy diagram presenting the principle behind inductively coupled plasma – optical emission spectrometry. a and b represent excitation, c is ionization, d is ionization/excitation, e is ion emission, f, g, h are atomic emissions. λ represents the wavelength of emission.

The relationship between the energy difference and wavelength can be derived through Pluck's equation:

$$E = h \cdot v \qquad \text{(Eq 15)}$$

Where E is the energy difference between two levels, *h* is Plack's constant and v is the frequency of the radiation.

4.1 **Instrument**

The ICP-OES instrument used in the project was an Agilent 5100. The main parts are: autosampler, nebulizer, spray chamber, torch and detector.

Figure 4-2: Inductively coupled plasma – optical emission spectrometer (Agilent 5100).

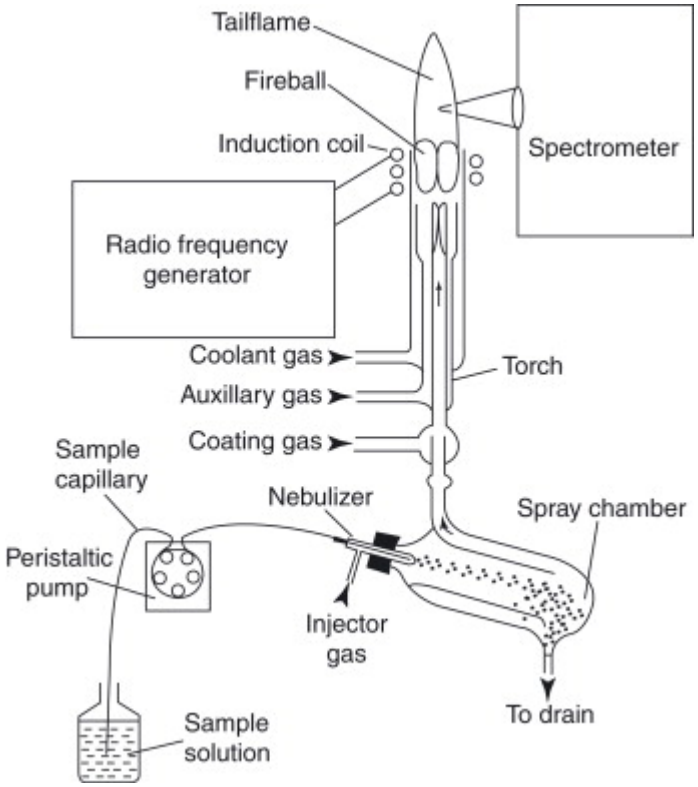


Figure 4-3: Schematic of the ICP-OES instrument[56].

4.1.1 **Torch**[57]

Torches used in an ICP-OES instrument contain three concentric quartz tubes which are sealed together. The torch used in the experiments was a G8010-60236, which is a plug-in type with 1.8mm internal diameter. The main disadvantages of this one-piece torch are that they are not resistant to corrosion by HF and if damaged, the entire torch must be replaced.

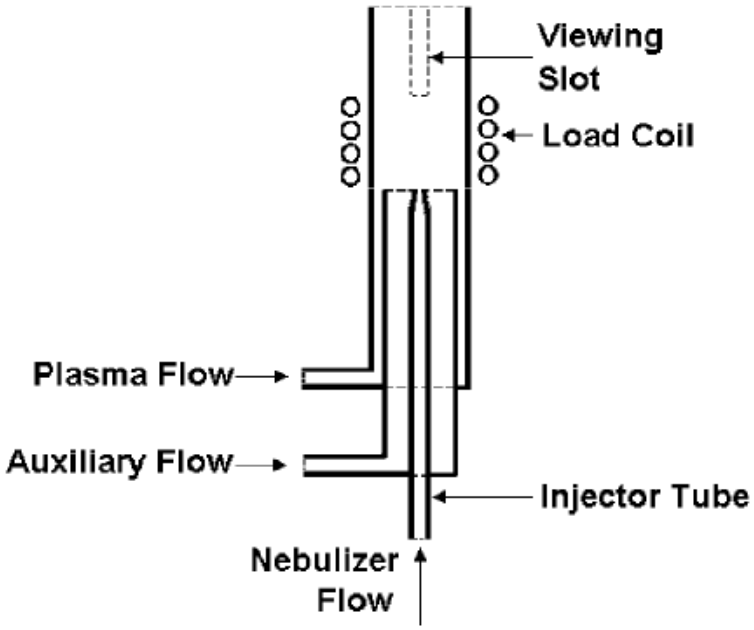


Figure 4-4: Schematics of a torch used in ICP-OES analysis[55].

4.1.2 **Plasma**[54,57,58]

Gas (usually argon) is injected into a high frequency generated magnetic field which creates an inductively coupled plasma. It forms a cloud of gaseous ions and high-energy electrons. A sample in form of an aerosol in presented to the plasma. Then the sample is completely broken down by the high temperature (approximately 9,000-10,000K) into the constituent atoms and ions.

The plasma has three different temperature zones, which are clearly seen while an yttrium sample is introduced (Figure 4-5). The blue zone is also called the analytical zone with the highest temperature which excites an element so the emitted photons can be detected. The dark red zone represents emission from atomic yttrium following desolvation, dissociation and atomisation of the aerosol. The coolest part of the plasma is the light orange coloured zone, representing emission from molecular species such as oxides of yttrium.

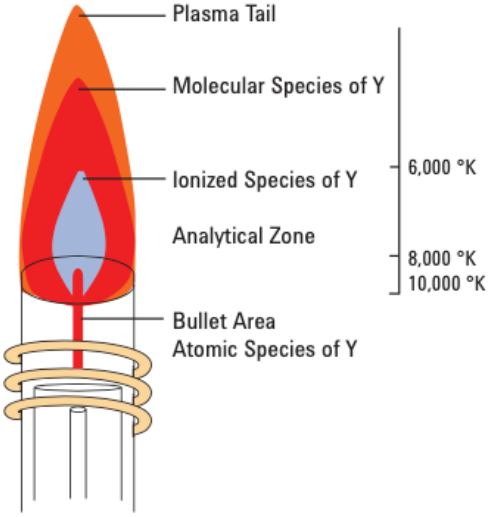


Figure 4-5: Plasma regions and temperatures as viewed while analysing a solution of 1000mg/l yttrium[57,58].

4.1.2.1 **Torch configuration**

There are two possible geometric detection views during the ICP-OES analysis. They are called axial or end-on viewing of the plasma and radial or side-on viewing of the plasma (Figure 4-6). There is also third possibility which combines the two previously mentioned, which is known as “dual view”.

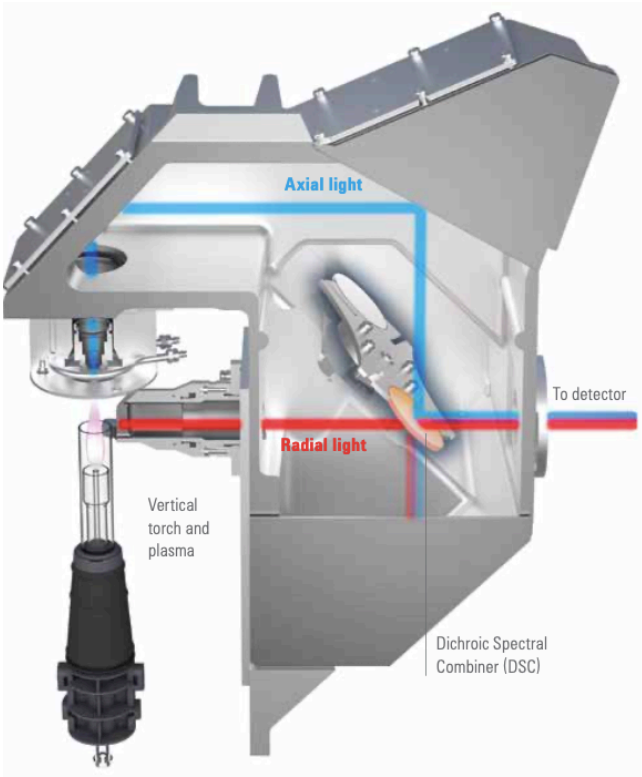


Figure 4-6: Schematic of radial and axial views of the sample in ICP-OES analysis[59].

4.1.2.2 **Radial view**

In the radial view, the analytical zone is observed from the side of the plasma. It constrains the observation volume to the distance through the diameter of the plasma. This path length is limited and so is the sensitivity. There is also the possibility of background interferences. The radial view allows for better linearity and less noisy determinations than the axial view orientation, which results in improved analytical precision.

4.1.2.3 **Axial view**

In axial view the signal is observed from end of the plasma. This view provides improved sensitivity, and thus lower LODs (5- to 10-fold improvement). It is possible because of the longer viewing path available down the plasma. The main disadvantages are increased potential for spectral interference and self-absorption effects caused by observation through the cooler tail plume of the plasma.

Both strategies present disadvantages including additional consumption of the gas or reduced capacity of handling samples with high amounts of suspended solids. Spectral interferences could be corrected or minimised by improving spectral resolution or by applying interelement correction factors.

4.1.2.4 **Dual view**

Many instruments combine both, axial and radial views into a single dual view. This allows analysis of very complex samples with a wide range of elemental concentrations. A reflective surface or periscope is required to collect the signals from both view orientations, thus at least two readings are necessary to cover both viewings of the plasma. An alternative is a dichroic spectral combiner (DSC) which combines data from both views at specific wavelengths. What is more, the synchronous dual view configuration allows detection of high concentration simultaneously with those at trace levels. It enables faster analysis and reduces argon consumption.

4.1.3 **Spray chamber**[55]

The spray chamber provides constant delivery of the fine-sized droplets produced by the nebulizer. It removes larger droplets which are not suitable for the analysis. Usually only droplets with a diameter of about 10µm or smaller are allowed to pass to the plasma.

Figure 4-7: Spray chamber used in the experiments.

4.1.4 **Nebulizer**[54,55]

The nebulizer is used as a sample introduction to the plasma, it converts a liquid sample into a fine aerosol. There are two types of nebulizers, pneumatic and ultrasonic. The high-speed gas is used to create an aerosol in pneumatic nebulizer and ultrasonic oscillations of a piezoelectric crystal in ultrasonic nebulizer. The nebulizer used in ICP-OES analysis, produces aerosol by the high-speed gas flow (argon).

4.1.5 **Radio frequency generator**

The radio frequency generator provides the power for the generation and sustainment of the plasma. Power output is between 700 and 1500W. It is transferred to the plasma gas through a load coil on the top of the torch. It operates at a frequency of 27MHz which gives reduced background emission. A radio frequency generator coupled with a vertical torch allows robust measurements of the variety of sample types.

4.1.6 **Wavelength dispersive device**

4.1.6.1 **Grating**

The most common way to isolate a particular emission wavelength is by using a diffraction grating. Most gratings have line and groove density from 600 to 4200 lines per millimetre.

When the light beam strikes the grating at the incident angle of α to the grating, it is diffracted into three different component beams at angles β, θ and ω (Figure 4-8). Generally, the longer the wavelength and the higher the groove density (lower *d*), the higher the angle of diffraction. In the ICP-OES instrument the grating is incorporated in the spectrometer. The main function of spectrometer is to provide only required wavelength to pass to the detector and block all the others.

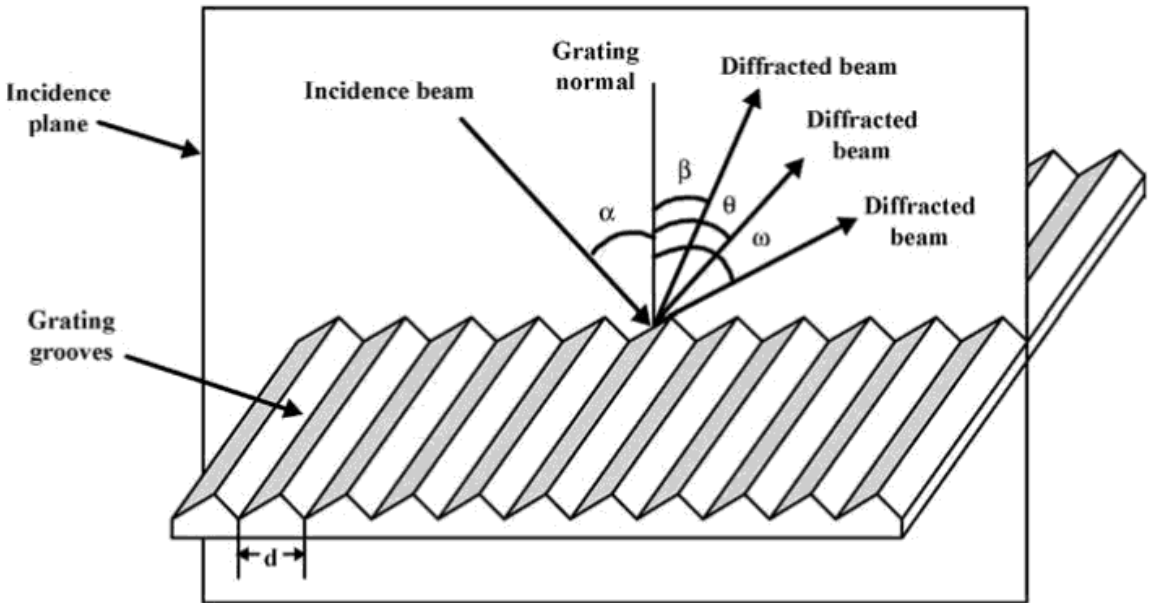


Figure 4-8: Light dispersion by a reflection diffraction grating.

4.1.6.2 **Monochromator**

The monochromator has only one exit slit and one detector. In multielement analysis, it requires rapid changes of the wavelengths. It is done by changing the angle of the diffraction gratings or rotation or movement of the detector (while leaving the grating in a fixed position). The most popular monochromators are Czerny-Turner and Ebert mounts (Figure 4-9). One can see that in the Czerny-Turner arrangement two mirrors are used, while the Ebert arrangement has one mirror for focusing the light into a single exit slit.

Monochromator-based systems have great spectral flexibility, they allow measurements at any wavelength in the range at any time. It also allows background corrections during the analysis of the complex background samples. The main disadvantages are sample volume required for the analysis and sample throughput.

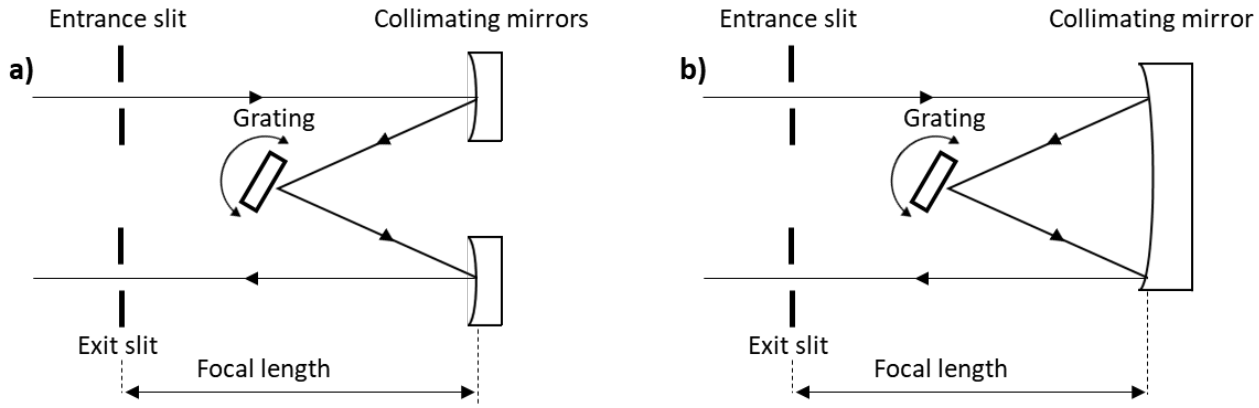


Figure 4-9: Monochromators a) Czerny-Turner and b) Ebert[55].

4.1.7 **Detector**

The detector used during the experiments was a CCD detector (charged-coupled device). In this particular ICP-OES instrument it was the VistaChip II detector. It provides full wavelength coverage from 167-785nm. ICP-OES allows determination of the 70 elements, that requires much higher resolution of 0.01nm or lower. The detector provides fast readout (about 0.8s) and has great sensitivity at all wavelengths (167-785nm).

The detector uses image mapping technology (I-MAP) to average more than 70,000 pixels that is required to cover all wavelengths. Blooming is the main issue associated with a large number of pixels. Blooming occurs when the spectral line saturates one or more detector pixels. It may lead to inaccurate results or the additional requirement that the measurement needs repetition, which makes analysis time longer. The VistaChip II detector has an antiblooming drain on each pixel which drains excess charge from the pixel, so it will not pass to the neighbouring pixels.

4.1.8 **Choosing wavelengths for the analysis**

All of the elements may be detected at various wavelengths. The key to the successful analysis is the choice of wavelengths. There are many available for each element. The main rule is to make

sure that there is no overlap while analysing multiple elements. Doing so may result in inaccurate results. The software used in the project highlighted the problematic wavelengths (Figure 4-10d). The second important feature is the emission intensity (Figure 4-10b). When choosing the element for the analysis there is a list of wavelengths with the expected response. Thus, it is possible to select the best wavelength for all analysed elements.

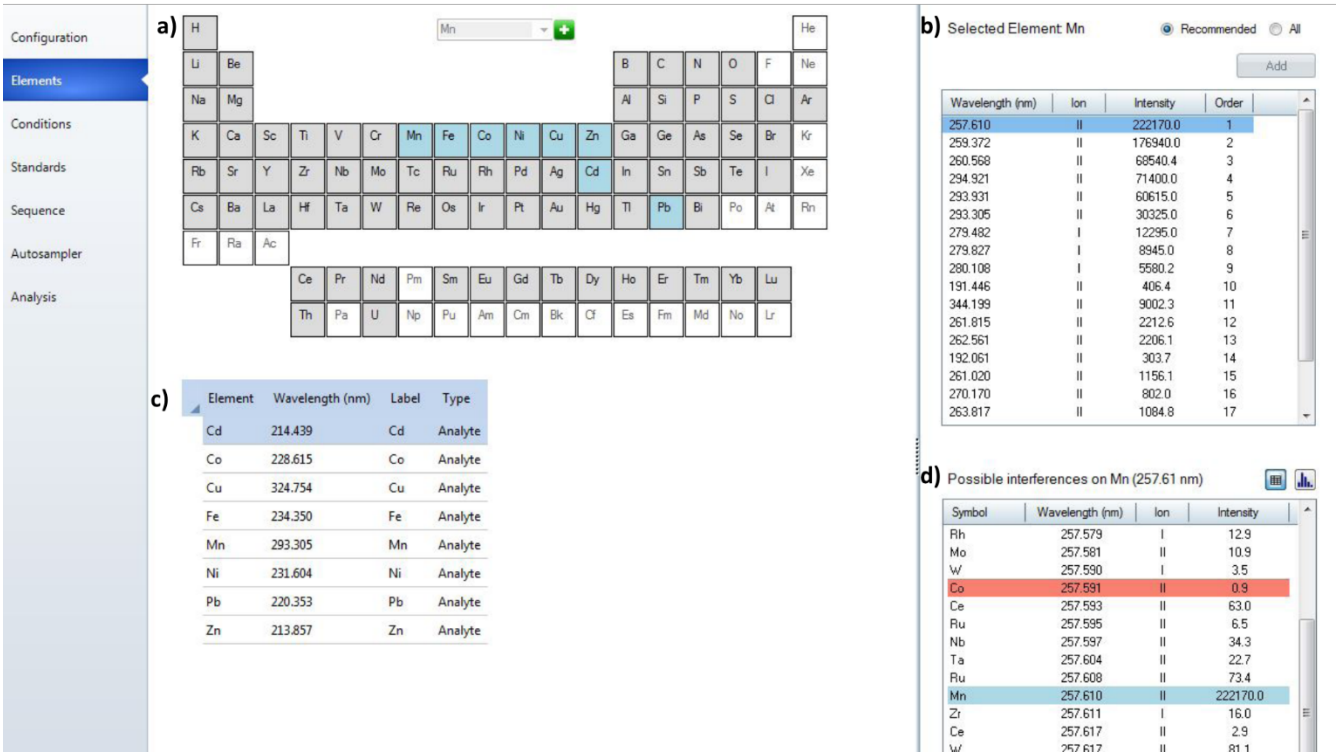


Figure 4-10: Choice of the wavelength in the software. a) periodic table used in the elements' selection; b) wavelengths available for analysis with expected intensity; c) chosen elements and wavelengths; d) possible interferences[60].

4.1.9 **Data analysis**

Software available for the ICP-OES instrument prepares calibration graphs for each analyte (Figure 4-11b) at the selected wavelength.

All samples are injected into the instrument by the autosampler. Example of the result is presented in Figure 4-11 and in the graph where the intensity is converted into concentration, based on the calibration graph.

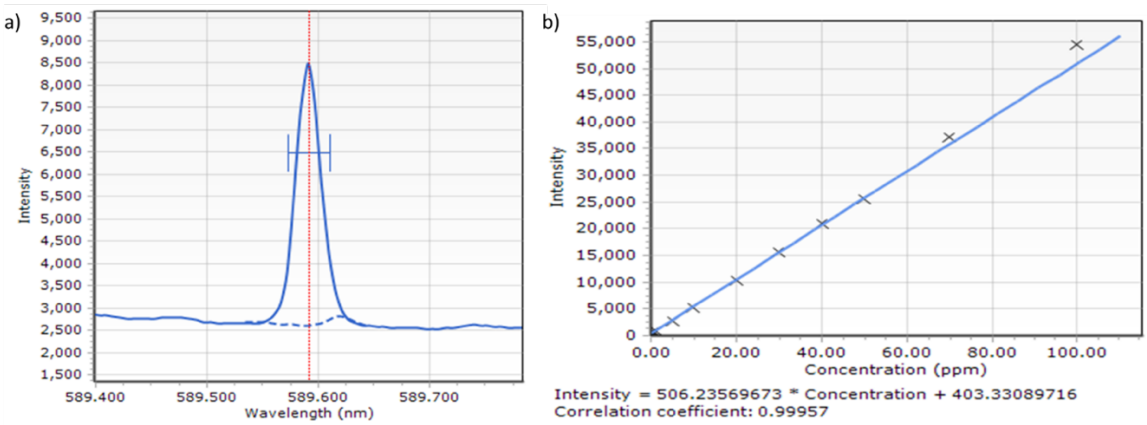


Figure 4-11: Examples of the results of ICP-OES analysis of sodium at 589.592nm. a) intensity at the chosen wavelength; b) calibration graph prepared for sodium.

4.2 Calibration of ICP-OES

All ions of interest were examined at multiple wavelengths in many experiments (Table 4-1). In most cases sample was analysed at two wavelengths per element per run. The calibration was conducted for standards with concentrations between 0.25 and 100 mg/l.

Table 4-1: Wavelengths used in analysis of the elements.

Wavelengths [nm]						
Al	**Ca**	**Cr**	**Cu**	**Fe**	**Mg**	**Pb**
226.910	315.887	205.560	204.380	234.350	202.582	217.000
236.705	317.933	206.158	213.598	238.204	277.983	220.353
308.215	318.127	266.602	217.941	238.863	279.078	280.199
309.271	370.602	267.716	218.172	239.563	279.553	283.305
394.401	373.690	276.623	219.227	240.489	279.800	363.957
396.150	393.366	276.653	222.778	258.588	280.270	405.781
396.152	396.847	28 3.563	222.887	259.940	283.230	
	422.673	284.325	223.009	261.187	285.213	
	430.253	286.674	224.700	261.382	293.651	
	612.222	313.205	324.754	262.567	383.829	
	616.217	357.868	327.395	234.830	383.230	
	643.907			259.837		

Chapter 5 Methods, chemicals and samples

5.1 Chemicals and samples used in the project

All standards and electrolytes were prepared using ultra-pure water available in the laboratory (Arium® pro UV by Sartorius). According to the manufactures' specifications ultra-pure water can be used in the majority of the chemical and analytical applications, such as: gas chromatography – mass spectrometry (GC-MS), atomic absorption spectroscopy (AAS), inductively couple plasma – optical emission spectroscopy (ICP-OES), ion chromatography (IC), high performance liquid chromatography (HPLC), photometry and total organic carbon (TOC) analysis.
The system is equipped with a UV lamp (185/254nm) to prevent microbiological growth, conductivity is maintained at 0.055µS/cm which is important in ITP analysis.

Standards for ion chromatography and isotachophoresis were prepared as the concentration of the ion of interest in each salt (see Table 5-1 for the calculations). All standards were prepared as 1,000mg/l of each ion and then diluted to the final concentration using ultra-pure water. For ITP, calibrations standards were prepared as a single ion solution to obtain the calibration graphs and the RSH for all ions and additionally as a mixture for the ions of interest. Ion chromatography only allowed separation of some ions analysed in the project, thus only these were present in the IC standards solutions (Ca^{2+}, Mg^{2+}, Na^{+}, NH_4^{+} and K^{+}).

For inductively coupled plasma - optical emission spectroscopy, standards with all elements of interest were prepared. In this technique the oxidation state is not detected.

To prevent transfer of ions from the glassware to the solutions (mainly sodium ions), polypropylene (PP) labware was used throughout the project, including volumetric flasks, beakers, test tubes and storage bottles.
Stock solutions of standards were prepared and stored for up to a few weeks. Cr^{3+} and Fe^{2+} ions can easily oxidize to different oxidation states when left for some time. This may result in inaccurate and misleading data. This problem was prevented by making up fresh standards of these two ions for each experiment. To reduce the volume of chemical waste all standards were prepared in small quantities (up to a maximum of 50ml).

5.1.1 **Standards**

- Ammonium chloride, NH_4Cl, ≥99.5%, Honeywell
- Ammonium sulphate, $(NH_4)_2SO_4$, ≥99.0%, Sigma Aldrich
- Aluminium chloride hexahydrate, $AlCl_3 \cdot 6H_2O$, 99%, Honeywell
- Calcium carbonate, $CaCO_3$, 99%+, Acros Organics
- Calcium chloride dihydrate, $CaCl_2 \cdot 2H_2O$, 99%+, Acros Organics
- Chromium (III) chloride hexahydrate, $CrCl_3 \cdot 6H_2O$, 99.5% min, Alfa Aesar
- Copper (II) chloride dihydrate, $CuCl_2 \cdot 2H_2O$, 99%+, Acros Organics
- Iron (II) sulphate heptahydrate, $FeSO_4 \cdot 7H_2O$, ≥99.0%, Honeywell Fluka
- Magnesium chloride, $MgCl_2$, pure, Acros Organics
- Lead (II) nitrate, $Pb(NO_3)_2$, 99%, Alfa Aesar
- Potassium chloride, KCl, ≥99.0%, Sigma Aldrich
- Sodium chloride, NaCl, laboratory grade, Fisher

Table 5-1: Calculation of masses of salts used to prepare standards.

		In 1 litre			**In 50 ml**
Salt	**Ion**	**Mass of salt [mg/mol]**	**Mass of ion [mg/mol]**	**Mass of salt for 1,000mg/l of ion [mg]**	**Mass of salt for 1,000mg/l of ion [mg]**
NH_4Cl	NH_4^+	53490	18039	2965.24	148.26
$(NH_4)_2SO_4$	NH_4^+	132140	36078	3662.62	183.13
$AlCl_3 \cdot 6H_2O$	Al^{3+}	241430	26982	8947.81	447.39
$CaCl_2 \cdot 2H_2O$	Ca^{2+}	174020	40078	4342.03	217.10
$CrCl_3 \cdot 6H_2O$	Cr^{3+}	266450	51996	5124.43	256.22
$CuCl_2 \cdot 2H_2O$	Cu^{2+}	170480	63546	2682.78	134.14
$FeSO_4 \cdot 7H_2O$	Fe^{2+}	278010	55845	4978.24	248.91
$Pb(NO_3)_2$	Pb^{2+}	331200	207200	1598.46	79.92
$MgCl_2$	Mg^{2+}	95210	24305	3917.30	195.87
KCl	K^+	74550	39098	1906.75	95.34
NaCl	Na^+	58440	22990	2542.97	127.10

Data from the Table 5-1 was obtained from the SDS sheet for the chemical or from a periodic table that included elemental mass data. Calculations of the mass of salt used to prepare 1,000 mg/l solutions were performed as follows:

$$mass\ of\ ion\ \left[\frac{mg}{mol}\right] \rightarrow mass\ of\ salt\ \left[\frac{mg}{mol}\right]$$

$$1{,}000\,\frac{mg}{mol} \rightarrow x$$

$$x = \frac{mass\ of\ salt * 1{,}000}{mass\ of\ ion}\ \left[\frac{mg}{mol}\right] \qquad \text{(Eq 16)}$$

Using (Eq 16) it is possible to calculate the amount of salt needed to prepare 1l of 1,000mg/l of ion standard. In the project such large volumes were not required thus all standards were prepared as 50 ml stock solutions. The following method was used to calculate the correct mass:

$$x\left[\frac{mg}{mol}\right] \rightarrow 1l$$

$$y\left[\frac{mg}{mol}\right] \rightarrow 0.05l$$

$$y = \frac{x * 0.05}{1}\ \left[\frac{mg}{mol}\right] \qquad \text{(Eq 17)}$$

5.1.2 **Electrolytes chemicals**

5.1.2.1 **Leading and terminating electrolytes**

- Ammonium hydroxide, 5.0M solution in water, Honeywell Fluka
- 1,3-Bis[tris(hydroxymethyl)amino] propane, 99%, Acros Organics
- Caesium hydroxide monohydrate, 96%, Alfa Aesar
- DL-carnitine hydrochloride, 99%, Acros Organics
- Lithium citrate hydrate, 97%, Aldrich
- Lithium chloride, 1M aqueous solution, Alfa Aesar
- 2-1-N-morpholino]ethane sulfonic acid (MES) hydrate, ≥99.5%, Sigma Aldrich
- Tetrabutylammonium hydroxide, 1.5M solution in water, Acros Organics
- Tris(hydroxymethyl)aminomethane, 99.8%, Acros Organics

5.1.2.2 **pH adjustments**

- Glycylglycine, 99%+, Acros Organics
- L-(-)-Malic acid, 99%, Alfa Aesar
- L-Histidine, 98%+, Alfa Aesar
- Propionic acid, 99%+, extra pure, Acros Organics
- Acetic acid glacial, Fisher Scientific
- α-Hydroxyisobutyric acid, 99%, Alfa Aesar
- β-Alanine, Sigma Aldrich

5.1.2.3 **Additives, electro-osmotic flow suppressor and complexing agents**

- 18-crown-6-ether, 99%, Acros Organics
- Hydroxyethyl-cellulose, viscosity 80-125cP, 2% in water, Sigma Aldrich
- Hydroxypropyl cellulose, M.W. 100,000, Alfa Aesar
- Kryptofix® 222, Sigma Aldrich
- Mowiol® 8-88 (Poly(vinylalcohol)), M.W. ~67,000, Sigma Aldrich
- Triton® X-100, Acros Organics

5.1.2.4 **Anionic dyes used in prototype evaluation**

- Bromophenol blue, BDH indicators
- Amaranth, 80%, Aldrich

5.1.2.5 **Other chemicals**

- 2-methoxyethanol. 99%+, extra pure, Acros Organics
- Eriochrome Black T, pure, indicator grade, Acros Organics
- Ethylenediaminetetraacetic acid disodium salt dihydrate, Na_2EDTA, 99.0-101.0%, Sigma Aldrich
- Sodium dodecyl sulfate, 92.5-100.5% based on total alkyl sulfate content, Sigma Aldrich

5.1.3 **Real samples**

Two types of real samples were analysed, bottled and tap water. The commonly available bottled waters in the UK were obtained. Tap water was sourced from different locations around the UK and Europe (Figure 5-1), so as to obtain a mix of hard and soft water.

There are no official standard levels to what constitutes a hard or soft water. However, the most common water hardness classification is shown in Table 5-2.

Table 5-2: Drinking water hardness levels[61].

Mg $CaCO_3$ [mg/l]	**Ca^{2+} [mg/l]**	**Hardness**
<50	<20	Very soft
50-100	20-40	Soft
100-200	40-80	Moderately hard
201-300	80.4-120	Hard
>300	>120	Very hard

All water samples were used to check the methods developed in the project. Comparison of the ions' concentrations from the label (for bottled waters) and from the official data from water providers are presented later in this study. Commercial analyses were done by:

- Thames Water Utilities Limited for London and Abingdon
- United Utilities for Lancaster, Rossendale and Stretford
- Nothumbrian Water for Durham
- Legnickie Przedsiebiorstwo Wodociagow i Kanalizacji (LPWiK) for Legnica
- Miejskie Przedsiebiorstwo Wodociagow i Kanalizacji (MPWiK) for Wroclaw

All the reports were available online and the latest version was used in preparation of the summary presented in Table 5-4. Unfortunately for some of the water samples the official data was not available as presented in table below.

Table 5-3: Measured pH and water hardness based on official information and measured levels.

		pH	Water hardness
Bottled water	Evian	6.94	Moderately hard
	Buxton	7.03	Moderately hard
	Highland Spring	7.05	Soft
	Tesco	7.41	Very soft
	San Pellegrino	6.6	Very hard
	Smartwater	7.39	Moderately hard
	Volvic	7.28	Very soft
	Sainsbury's	7.32	Soft
Tap water	London	7.92	Hard
	Durham	7.69	Soft
	Stretford	7.74	Very soft
	Rossendale	7.9	Very soft
	Legnica	7.36	Moderately hard
	Wroclaw	7.41	Hard
	Maybole	7.82	Very soft
	B-floor, Lancaster University	8.05	Very soft
	Abingdon	8.3	Hard
	Sicily	7.63	Moderately hard
	Turkey	7.56	Moderately hard
	Crete	7.72	Soft
	Toulouse	8.03	Soft

All samples were tested for all ions analysed in the project, however the majority of the ions are undetectable due to being present at very low concentrations.

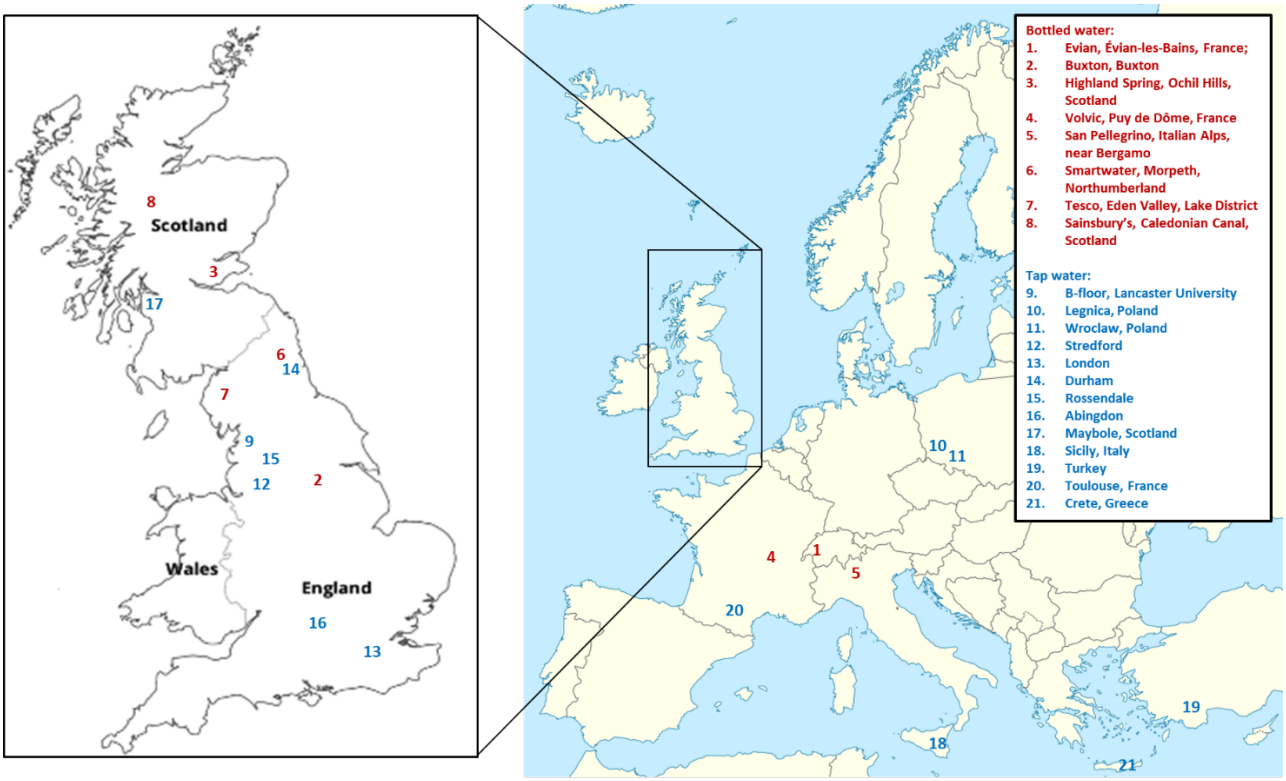


Figure 5-1: Map showing the origin of the samples – bottled water in red and tap water in blue.

Table 5-4: Concentrations of ions available on the bottle label or official reports for the water samples used in this study.

		Ion concentration [mg/l]								
		Ca^{2+}	Mg^{2+}	Na^{+}	NH_4^{+}	Al^{3+}	Cu^{2+}	Cr^{3+}	Fe^{2+}	Pb^{2+}
Bottled water	Evian	80	26	6.5	—	—	—	—	—	—
	Buxton	55	19	24	—	—	—	—	—	—
	Highland Spring	40.5	10.1	5.6	—	—	—	—	—	—
	Tesco	55	16	15	—	—	—	—	—	—
	San Pellegrino	164	49.5	31.2	—	—	—	—	—	—
	Smartwater	—	—	—	—	—	—	—	—	—
	Volvic	12	8	12	—	—	—	—	—	—
	Sainsbury's	11	3.5	10	—	—	—	—	—	—
Tap water	London	32.8	4.85	35.8	0.19	0.009	0.093	0.0009	0.003	0.006
	Durham	23	—	8.24	0.007	0.04	0.0196	0.0007	0.014	0.0003
	Stretford	10.4	1.76	9.01	—	0.012	0.039	—	0.007	0.003
	Rossendale	6.88	2.16	22.8	—	0.004	0.039	—	0.016	0.0006
	Legnica	81	14	—	0.06	—	—	—	0.02	—
	Wroclaw	82.2	10.3	—	—	—	—	—	0.02	—
	Maybole	10.78	0.73	5.43	0.21	0.003	0.00	0.0002	0.005	0.0005
	B-floor, Lancaster University	11.3	1.52	14.1	—	0.013	0.0054	—	0.061	0.003
	Abingdon	29.7	2.65	22.33	0.03	0.009	0.12	0.001	0.002	0.0003
	Sicily	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	Turkey	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	Crete	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	Toulouse	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

Chapter 6 Group 1 and 2 metal ions

6.1 Determination of water hardness

The main focus of the project was on the separation and determination of transition metal ions, but the ions responsible for water hardness were closely investigated as well, since the measurement of water hardness is of significant importance within the water industry, and therefore commercial interest of the project sponsors (Process Instruments Ltd.).

There are a few techniques available to measure water hardness in water samples. Some of them are quick and easy, others require some hazardous chemicals and take significant time. The most popular techniques are: colorimetric titration and water test kits.

In the analysis of water hardness different units for hardness are available. Depending on the country of origin, units may differ. According to ISO 6059-1984 the units conversion is as seen in Table 6-1.

Table 6-1: Water hardness unit conversion.

	Unit abbreviation	Molar concentration [mM/l of $CaCO_3$]	Concentration [mg/l of $CaCO_3$]
English hardness	°Clark	0.143	14.3
German hardness	°DH	0.178	17.8
French hardness	°f	0.1	10
U.S. hardness	ppm $CaCO_3$	0.01	1

6.1.1 Colorimetric technique

The technique widely used in laboratories for the measurement of water hardness is the colorimetric technique. It uses titration to measure water hardness, to yield the total of calcium (II) and magnesium (II) ions. It is used in the analysis of drinking, surface and industrial waste waters, however the technique is not applicable to waters with a high salt concentration such as seawater. The concentration of $CaCO_3$ detected using this technique is between 5-800mg/l. For lower concentrations a larger sample volume is required (up to 1000ml).

In some cases, the colorimetric technique is coupled with conductivity or a spectrometry detector to give more precise results.

6.1.1.1 **Method for colorimetric determination of water hardness**[62]

The indicator (Eriochrome Black T) turns red when in contact with calcium or magnesium in an alkaline solution at pH~10.0 and blue when cations are sequestered by EDTA (Figure 6-3). The sample is buffered to a pre-set pH, the indicator is added and forms a red complex with calcium and magnesium ions in the sample. The EDTA titrant reacts first with the free Ca^{2+} and Mg^{2+}, then with those bound to the indicator, causing the colour change to blue (Figure 6-2).

In a titration, EDTA is a stronger complexing agent than the indicator, so displaces the indicator from the metal ion allowing the indicator to turn to a pure blue colour (indicating the end point of the titration):

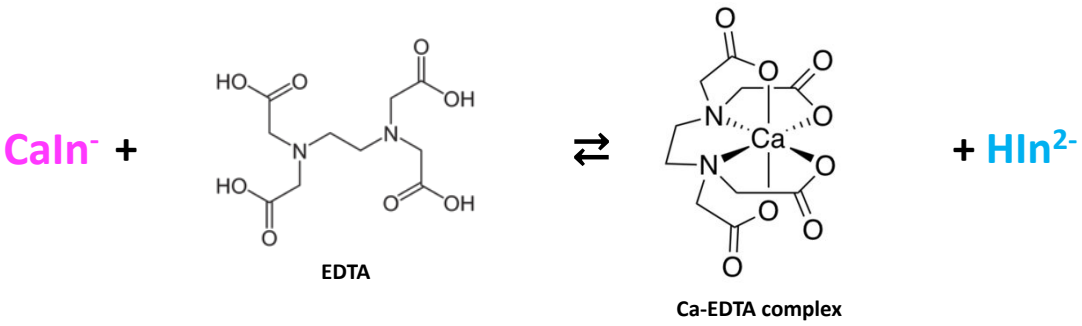


Figure 6-1: Complex formation between calcium ions and EDTA in the presence of an indicator.

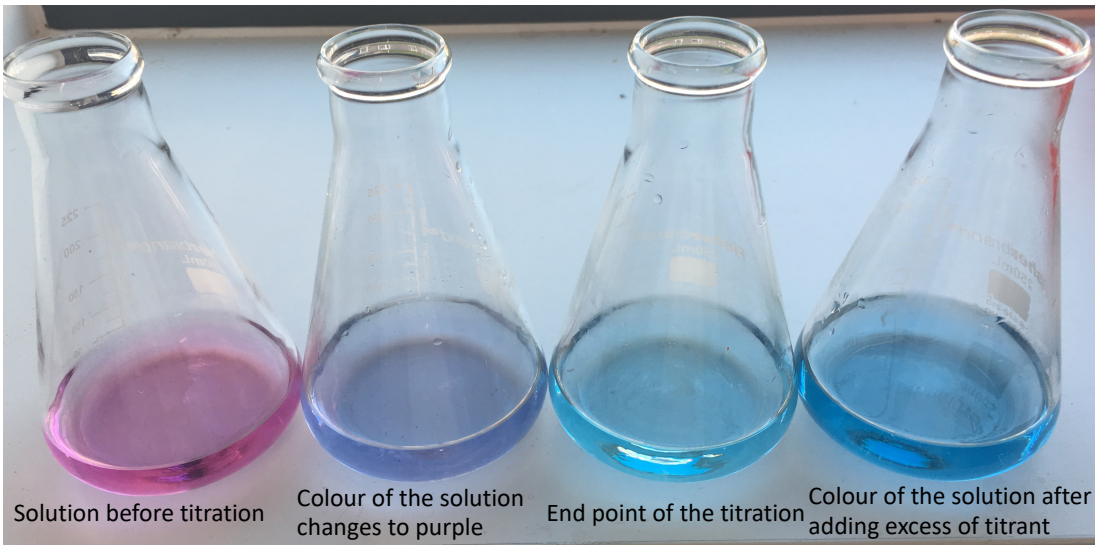
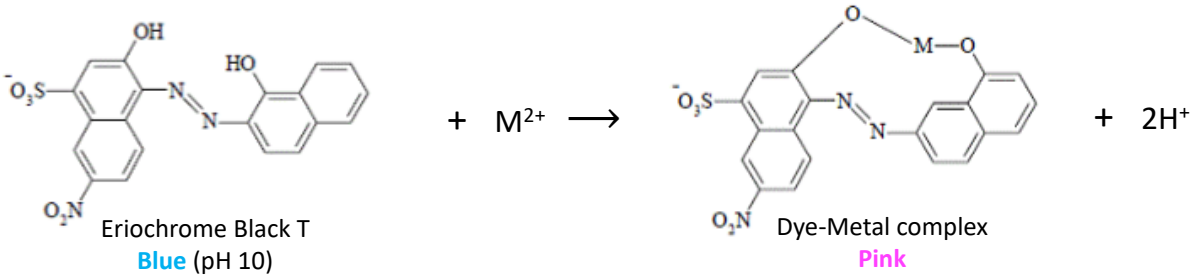


Figure 6-2: Colour change during Na_2EDTA titration in water hardness determination. From the left: pink before titration to blue at the end point.

Eriochrome Black T is used in complexometric titrations, such as titrations with EDTA in water hardness determination (Figure 6-3). pKa values for the dye used in the experiment are 6.6 and 11.6 respectively. For the conducted experiment, pH 10 or above, gives the expected colour change when titrated against EDTA.



Eriochrome Black T
Blue (pH 10)

Dye-Metal complex
Pink

Figure 6-3: Reaction between Eriochrome Black T dye and a metal ion during the titration process.

6.1.1.2 **Results analysis**

According to the method used, calculation of water hardness (expressed as: mg of $CaCO_3$ per litre) is calculated as follows:

$$hardness = \frac{V_t \cdot B \cdot 1000}{V_s} \qquad \text{(Eq 18)}$$

where V_t is volume of titrant [ml], B is mass [mg] of $CaCO_3$ equivalent to 1.00ml of EDTA and V_s is volume of sample [ml] which equals 25ml for all of the analyses.

To calculate the B value used in the equation above, titration of standard $CaCO_3$ solution was carried out. B value is calculated as follows:

$$B\ \frac{mg}{ml} \rightarrow 1.00\ ml\ of\ titrant$$

$$1\ \frac{mg}{ml} \rightarrow 23.9\ ml\ of\ titrant$$

$$B = \frac{1 \cdot 1}{23.9} = 0.042\ \left[\frac{mg}{ml}\right]$$

23.9 ml is the average of the titrant used in the analysis of 1ml = 1.00 mg standard $CaCO_3$ (Table 6-2).

Table 6-2: Results for titration of $CaCO_3$ standard.

Sample	Volume of titrant [ml]			
	First	Second	Third	Average
$CaCO_3$ standard 1	23.8	23.6	23.8	23.73
$CaCO_3$ standard 2	24.0	23.9	23.8	23.90
$CaCO_3$ standard 3	24.2	23.9	24.1	24.07
Total average				23.9

Example of calculation of hardness for Stretford's tap water sample:

$$hardness\ [mg\ CaCO_3] = \frac{0.93 \cdot 0.042 \cdot 1000}{25} = \underline{1.562}$$

In the determination of water hardness, various water samples were used. Details about the samples are available in section 5.1.3.

Table 6-3: Calculation of the concentration of $CaCO_3$ in the water samples using Eq 18).

Sample	Volume of titrant [ml]				B value	Concentration [mg $CaCO_3$]
	First	Second	Third	Average		
B-floor, Lancaster University	0.7	0.8	0.8	0.77	0.042	1.29
Wroclaw water	6.8	6.7	-	6.75		11.3
Stretford's tap water	0.7	1.1	1.0	0.93		1.56
Evian	7.7	7.6	7.5	7.6		12.8
Buxton water	5.1	5.3	5.1	5.17		8.68
Highland Spring	4.2	4.3	4.3	4.27		7.17
Volvic	1.2	1.4	1.4	1.33		2.24
San Pellegrino	15.0	15.2	15.2	15.13		25.4
Smartwater	4.0	4.1	3.9	4.00		6.72

6.1.2 Water test kits

6.1.2.1 Strip-based kits

There are many commercially available strip-based kits to estimate water hardness, mostly to use at home or in aquaria water analysis. The hardness is determined as a colour change. The advantage of them is that they are relatively inexpensive (~£10 per 100 strips), quick and easy to use, perfect to use where the accurate result is not needed. One just needs to dip the test stick in water for 3s and compare the colour to the colour chart provided by the manufacturer. They have a wide range, between 0-1000ppm, it is also worth mentioning, that this feature makes the test sticks useful in the analysis of both, soft and hard water.

The main weakness of the strips is that the intervals between colours are not equal and therefore a precise estimation of total water hardness is impossible (Figure 6-4). Some more accurate strips are available, however the colour change is harder to determinate because it is only based on colour intensity (Figure 6-5).

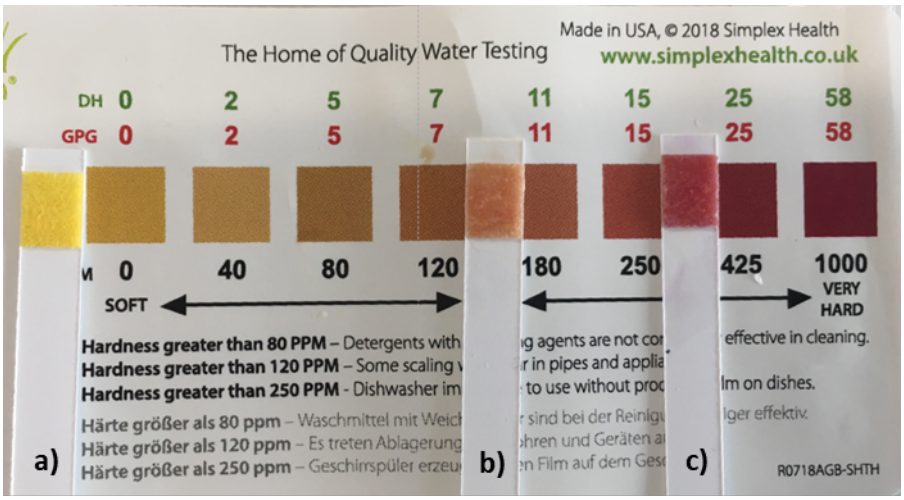


Figure 6-4: Strip-based kit for water hardness measurements (£12.99 per 100 strips). a) unused strip, b) analysis of soft water, c) analysis of hard water.

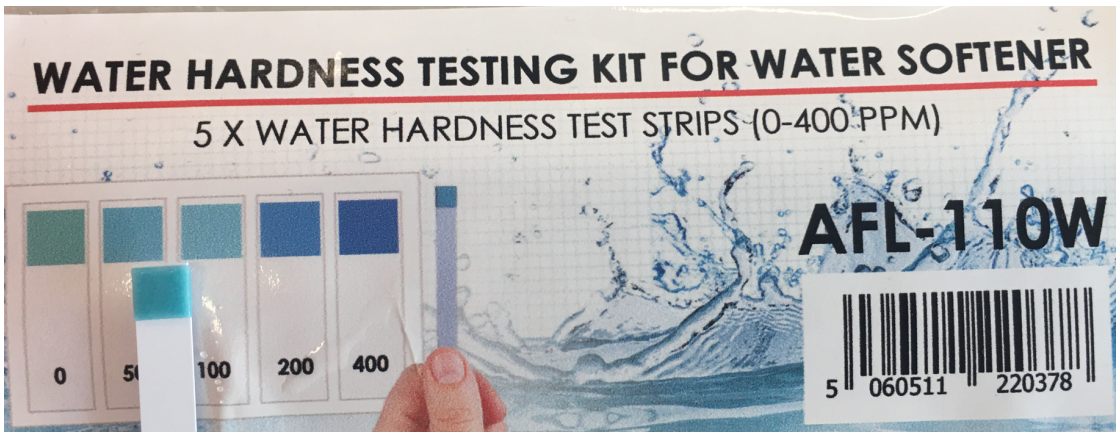


Figure 6-5: Strip-based kit for water hardness determination (FilterLogic).

Table 6-4: Results of water analysis using strips shown in Figure 6-4 for water hardness determination.

Sample	Water hardness [ppm]
Tap water (B-floor lab)	40-80
Wroclaw water	250-425
Stretford tap water	120-180
Evian	425-1000
Buxton water	425-1000
Highland Spring	180-250
Volvic	120-180
San Pellegrino	425-1000

6.1.2.2 **Titration-based kits**

Titration based kits are widely available on the market, their main usage is in aquaria and pond water samples. The kit presented in Figure 6-6 is based on a titration method. To perform the test, just 5ml of water sample is needed. Then 2 drops of regent GH A are added (solution changes colour to pink). To determinate water hardness of the sample addition of reagent GH B is required drop by drop, until the colour of the solution changes from pink to blue. The number of drops required for the colour change correspond to water hardness. In the kit used, 1 drop=1°DH. Samples were analysed using the titration-kit method, the results are presented in Table 6-5.

Figure 6-6: a) Titration-based kit for hardness water determination (£8.99 for kit allows analysis of up to 50 samples), b) soft water examination, c) hard water examination.

Table 6-5: Calculation of water hardness using method from the commercially available kit.

Sample	Analysis (number of drops)				Hardness concentration [°DH]	Hardness concentration [mg/l]
	First	Second	Third	Average		
B-floor lab, Lancaster University	1	1	1	1.00	1.00	17.8
Streford water	3	3	3	3.00	3.00	53.4
Wroclaw water	16	17	17	16.70	16.70	297
Evian	19	18	18	18.33	18.33	326
Buxton water	12	11	11	11.33	11.33	201
Highland Spring	10	12	11	11.00	11.00	196
Volvic	6	5	4	5.00	5.00	89.0
San Pellegrino	18	16	16	16.67	16.67	297

6.1.3 Isotachophoresis

Isotachophoresis is a perfect method for determination of calcium and magnesium concentrations in water samples. The majority of the industrial techniques report water hardness as combined concertation of calcium and magnesium. Isotachophoresis on the other hand, allows separation of the ions responsible for water hardness and calculation of the specific concentrations of the components (Ca^{2+} and Mg^{2+}).

Table 6-6 presents the ITP methods used for calcium and magnesium analysis. Method 21, 26 and 48 refer to Table 2-4 which presents electrolyte systems used in the separations. The table below summarises all analyses proving that the technique is reliable and gives consistent results which may be used to determine concentrations in the real samples.

Table 6-6: List of the methods used for ITP calibration in water hardness analysis.

Method	Ion	RSH (st dev)	R^2	Concentration [mg/l]	n
21	Ca^{2+}	0.489 (0.003)	0.9946	5-50	19
	Mg^{2+}	0.739 (0.006)	0.9987	5-50	19
26	Ca^{2+}	0.109 (0.003)	0.9951	2.5-100	36
	Mg^{2+}	0.143 (0.004)	0.9986	5-100	33
48	Ca^{2+}	0.496 (0.004)	0.9952	2.5-50	21
	Mg^{2+}	0.542 (0.006)	0.9979	0.25-50	30

Table 6-7: Step length [s] data from analysing different Ca:Mg ions mixtures using three electrolyte systems.

	Method 21			**Method 26**			**Method 48**		
%Ca:Mg	**Ca**	**Mg**	**Ca+Mg**	**Ca**	**Mg**	**Ca+Mg**	**Ca**	**Mg**	**Ca+Mg**
100:0	21.52	—	21.52	21.08	—	21.08	64.16	—	64.16
80:20	15.14	5.62	20.76	22.78	1.06	23.84	58.42	24.78	83.20
60:40	13.02	13.76	26.78	12.54	11.12	23.66	31.36	45.00	76.36
50:50	11.02	14.02	25.04	9.34	14.98	24.32	29.92	54.30	84.22
40:60	9.58	18.52	28.10	7.16	17.64	24.80	24.46	68.32	92.78
20:80	5.76	24.58	30.34	5.32	25.50	30.82	11.14	89.78	100.92
0:100	—	33.32	33.32	—	33.14	33.14	—	128.18	128.18

All three systems used in the isotachophoresis analysis of mixtures of calcium and magnesium ions, have some advantages and disadvantages. From the analysis of isotachopherograms it is possible to notice that the relative step heights (RSH) of ions are significantly different between the different electrolyte systems (

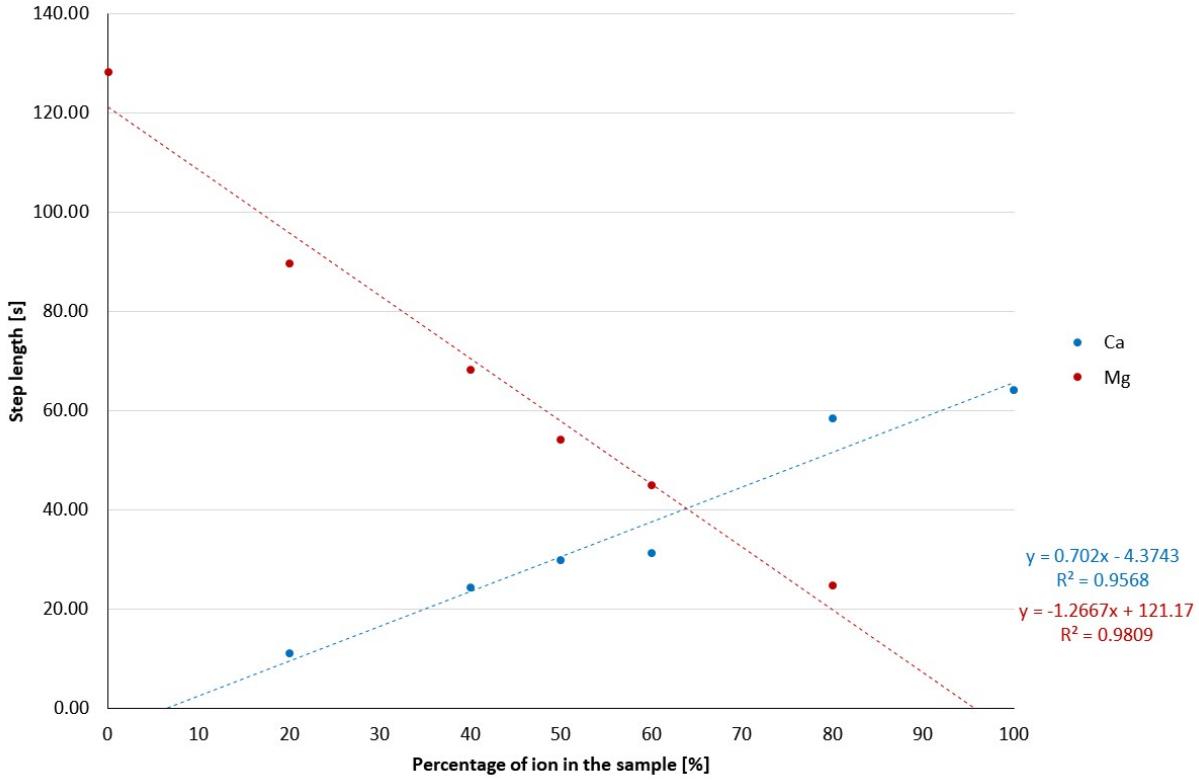


Figure 6-9a, c, e). The greater the difference in RSH, between Ca^{2+} and Mg^{2+} the easier the analysis of the separation. Based on that, the electrolyte system number 21: LE: 10mM CsOH (pH 9.0 by histidine), TE: 10mM lithium citrate, gives the best step resolution (RSH of Ca^{2+} 0.506 and Mg^{2+} 0.742). In system number 48 with LE: 10mM HCl, 0.05% Mowiol, TE: 10mM Tris), the difference is RSH is smaller (RSH of Ca^{2+} 0.513 and Mg^{2+} 0.574). An even smaller difference in RSH is found in electrolyte system number 26 consisting of: LE: 20mM NH_4OH, 10mM HIBA, 0.2% HPC (pH 4.8 acetic acid), TE: 10mM carnitine hydrochloride, RSH of Ca^{2+} 0.136 and Mg^{2+} 0.173.

The separation time is different in all analyses, the system using a LE of CsOH and TE of lithium citrate (Method 21) yields the separation in about 360s for the analysis of a mixture of calcium and magnesium ions. The same experiment takes approximately 690s for the separation when using a LE consisting of ammonium hydroxide, HIBA and HPC and a TE of carnitine

hydrochloride (Method 26). An even longer separation time, up to 1000s, is required when using the simplest electrolyte system (LE HCl, mowiol and TE Tris – Method 48).

Graphs presented in

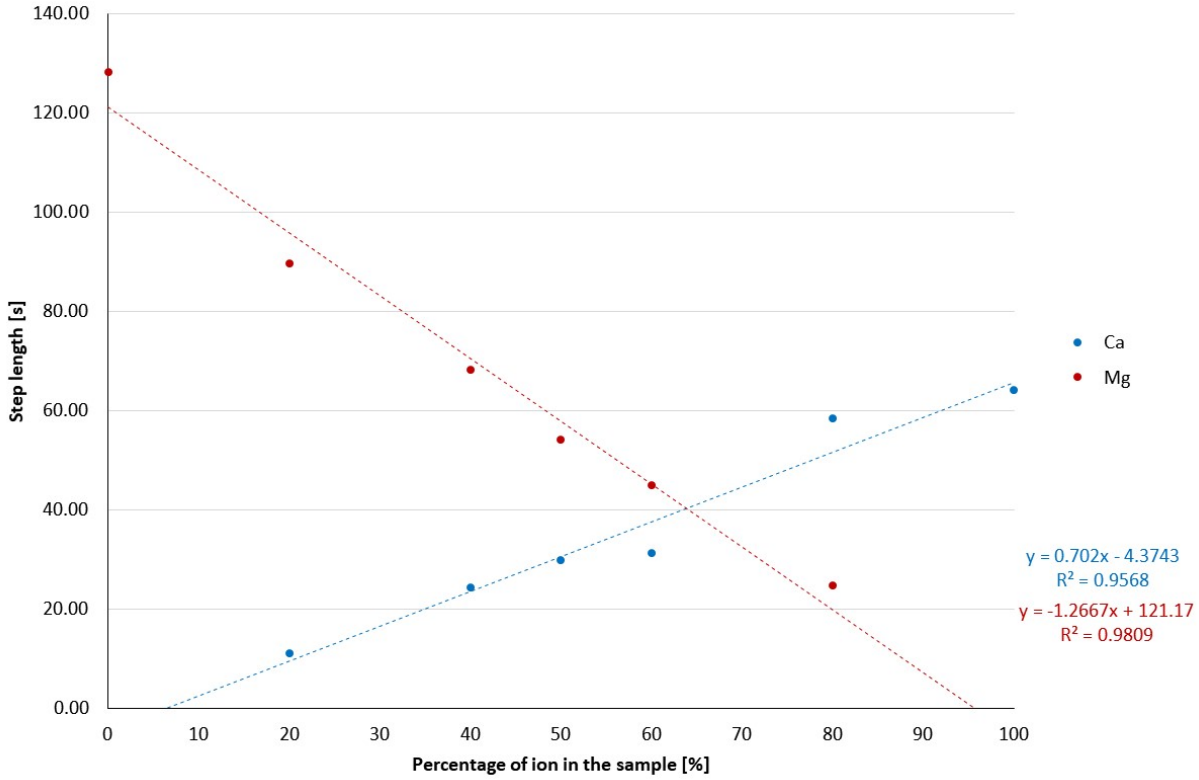


Figure 6-9b, d and f show how the step length of each ion changes when the sample composition changes. In all cases, results are as expected, the lower the concentration, the shorter the step. Good linearity with a correlation coefficient of ≥0.95 is evidence of the reproducibility of all the systems. The only exception is calcium analysis by the separation system consisting of LE ammonium hydroxide, HIBA and HPC, and TE carnitine hydrochloride, where the correlation coefficient equals 0.88.

It has been found that the chemicals used in the electrolyte systems have some additional influence on the choice of separation systems. In the caesium hydroxide separation system, citrate salt used as the terminating electrolyte may promote mould formation in the electrolyte solution, so preparation of a new solution every day or UV sterilisation may be required. Chemicals used are relatively expensive, so the preparation of a new leading electrolyte and pH adjustments required every day of the analysis increase the operation expense.

Ammonia solution used as a leading electrolyte solution is potentially hazardous, it may cause skin burns, respiratory irritation, and eye damage, and is harmful to aquatic life so the disposal is not easy. Also, ammonia-based electrolytes tend to lose ammonia, and thereby change in composition with time. Hydroxypropyl cellulose, used as an electro-osmotic flow suppressor, is hard to dissolve in water. The pH of the LE needs to be adjusted before every analysis, so a new solution is required for every analysis.

The simplest system consists of hydrochloric acid and mowiol as the leading electrolyte and tris(hydroxymethyl)aminomethane as the terminating electrolyte (Method 48). The chemicals used are relatively inexpensive and no pH adjustment is required. This method gives the longest steps for both ions, so samples with lower concentrations of ions may be analysed with greater precision.

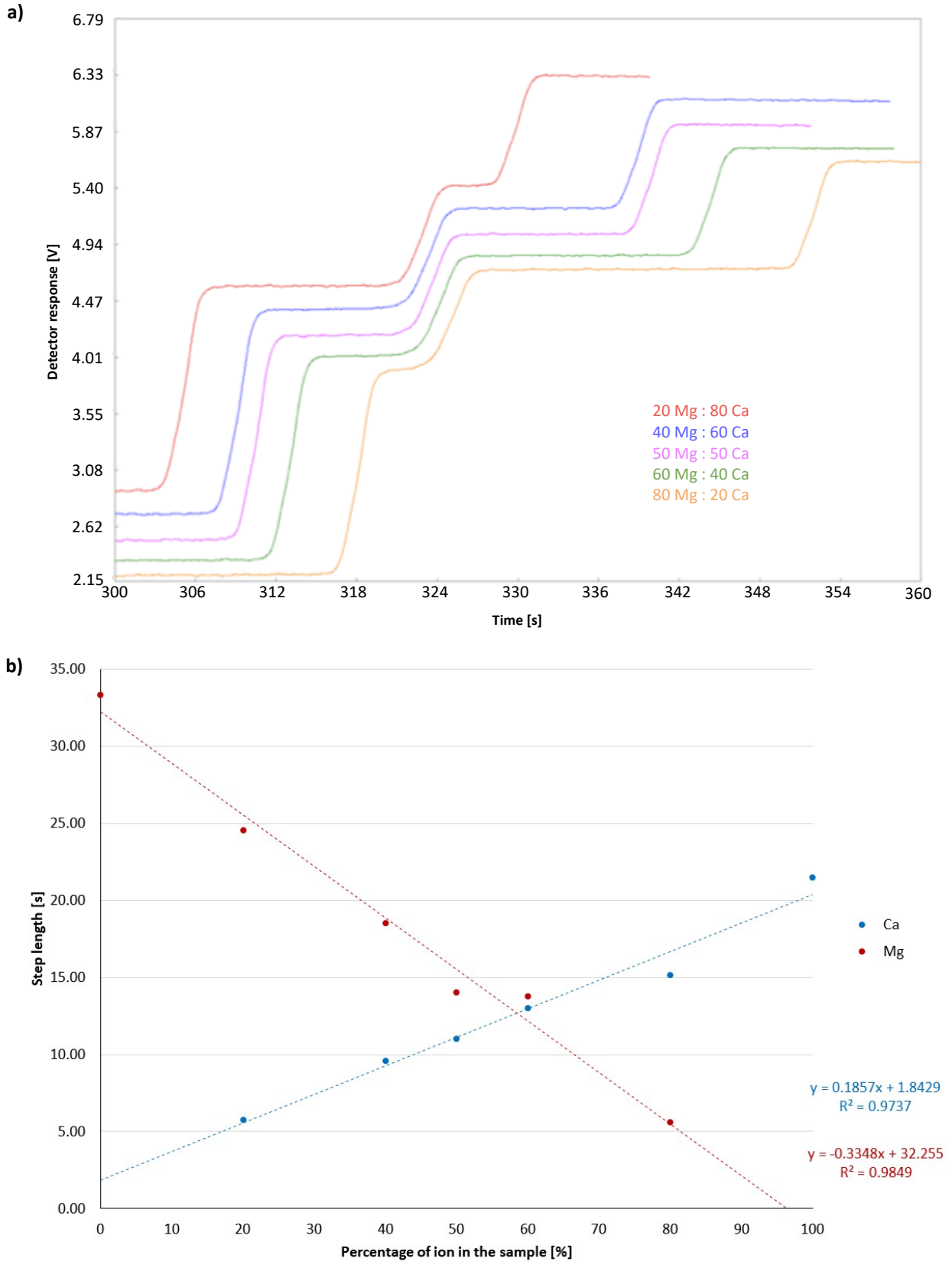
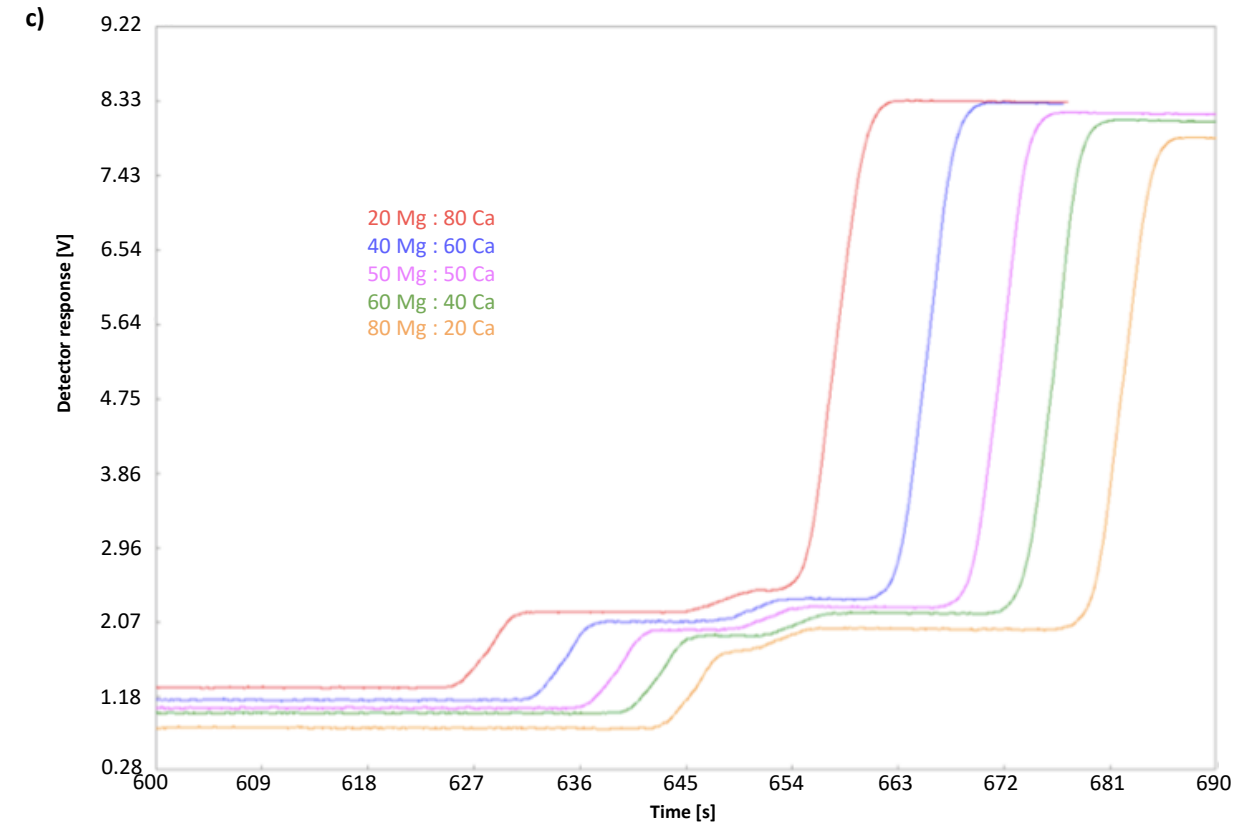


Figure 6-7: Analysis of mixtures of calcium and magnesium ions for water hardness determination. Colours of the graphs represent different concentration of calcium/magnesium in the sample. The following electrolyte systems were used in the analyses: a) and b) LE: 10mM CsOH, pH 9.0 (histidine), TE: 10mM lithium citrate (Method 21).



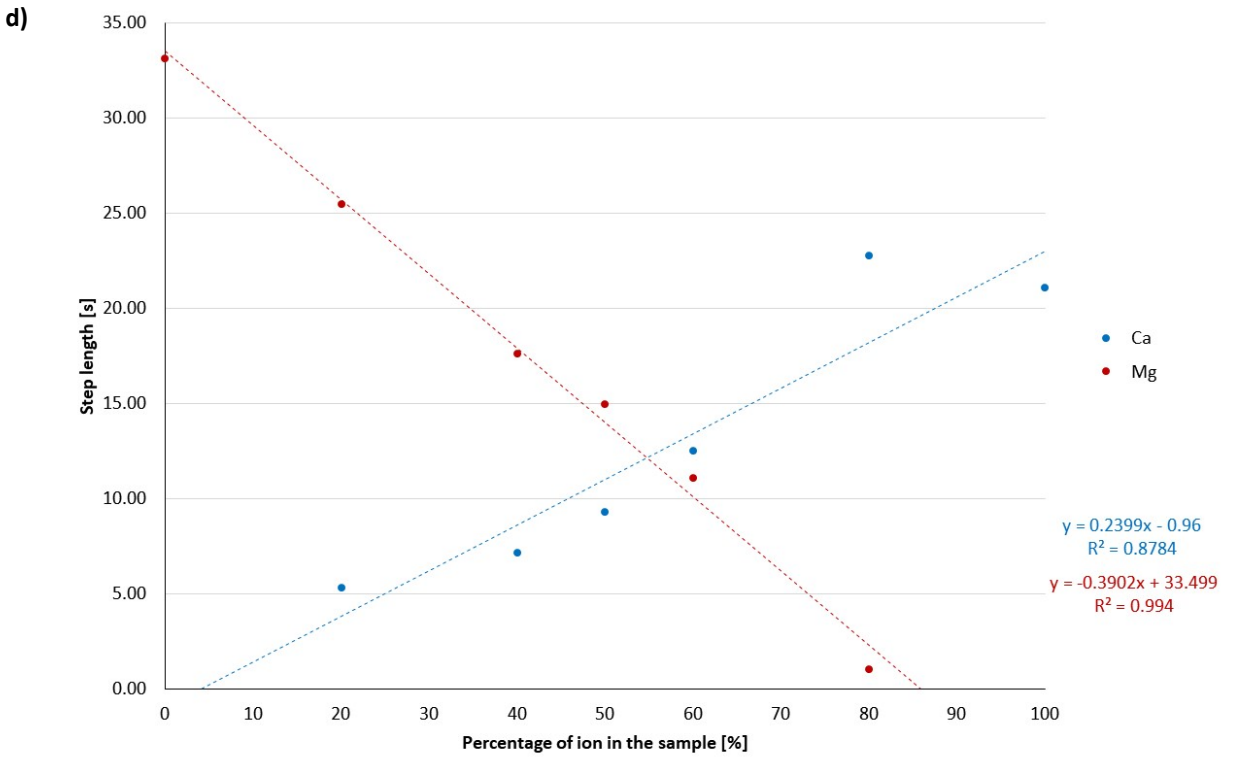


Figure 6-8: Analysis of mixtures of calcium and magnesium ions for water hardness determination. Colours of the graphs represent different concentration of calcium/magnesium in the sample. The following electrolyte systems were used in the analyses: c) and d) LE: 20mM NH_4OH, 10mM HIBA, 0.2% hydroxypropyl cellulose (HPC), pH 4.8 (acetic acid), TE: 10mM carnitine hydrochloride (Method 26).

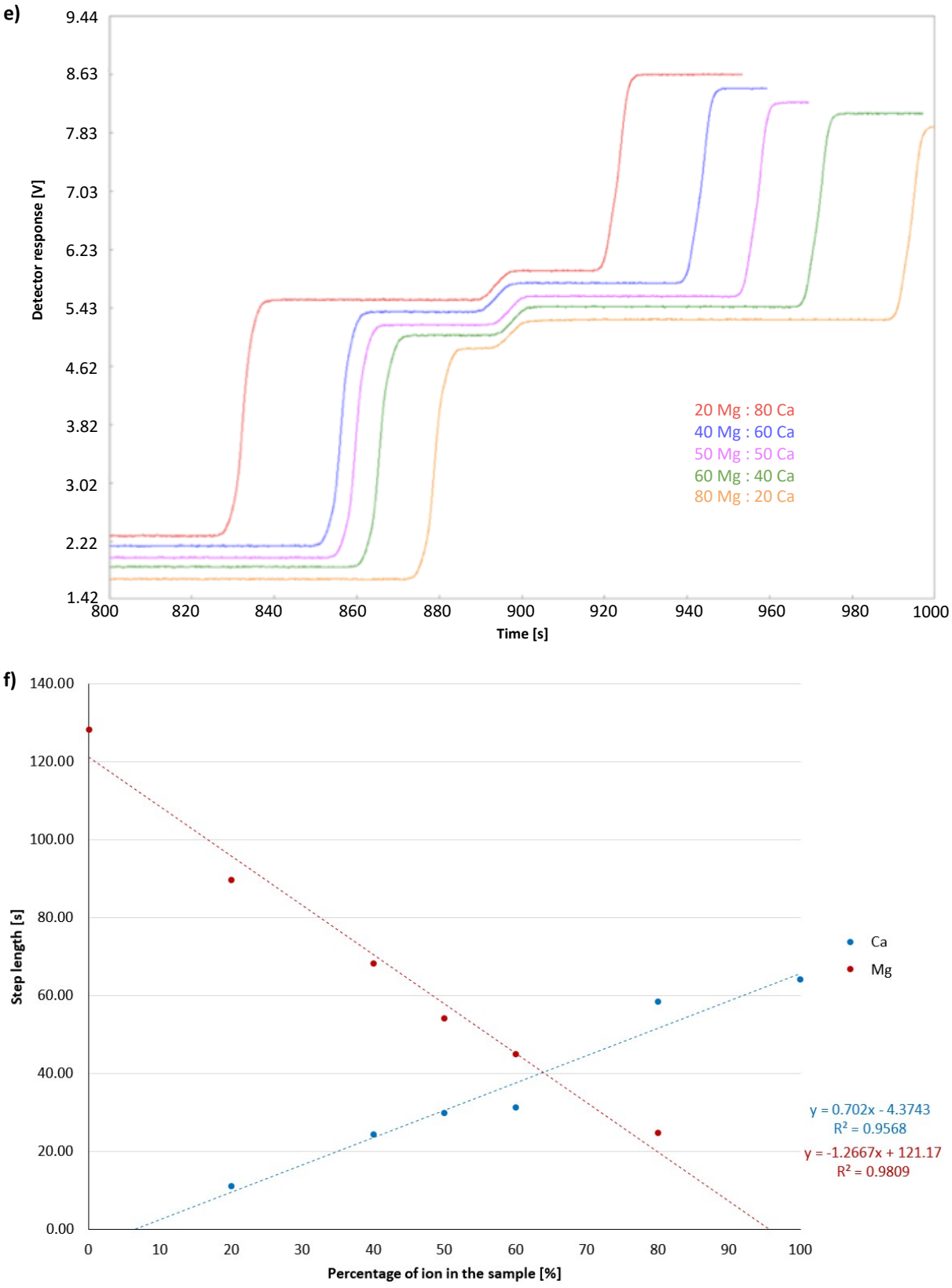


Figure 6-9: Analysis of mixtures of calcium and magnesium ions for water hardness determination. Colours of the graphs represent different concentration of calcium/magnesium in the sample. The following electrolyte systems were used in the analyses: e) and f) LE: 10mM HCl, 0.05% Mowiol, TE: 10mM Tris (Method 48).

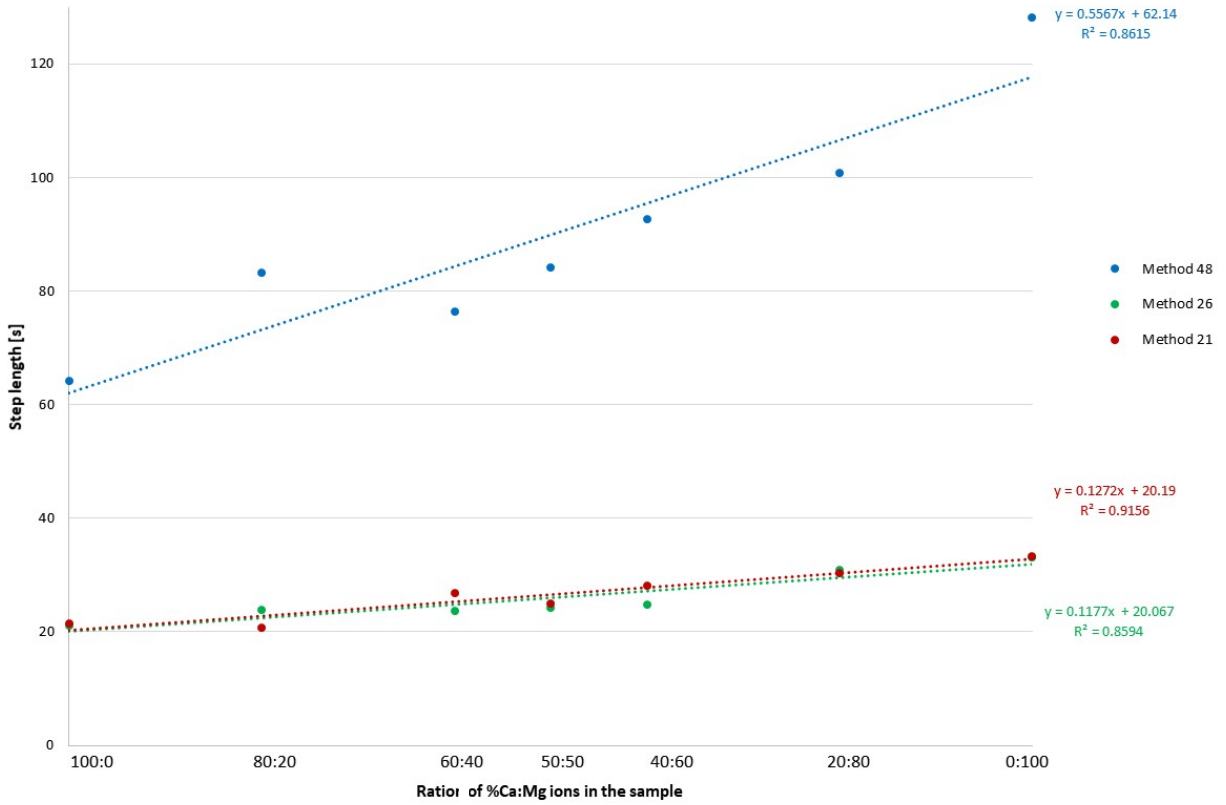


Figure 6-10: Graph showing the relationship between sample composition and step length in calcium and magnesium ions mixture analysis (based on Table 6-7).

The data was plotted to check if there is a trend in the combined step length of two ions, calcium and magnesium, in water hardness analysis. It is possible to clearly see the trend, with R^2 values <0.8. Method 48 gives the longest steps for both ions however the data shows some inconsistency. That may be due to the electrolyte system which does not require pH adjustment.

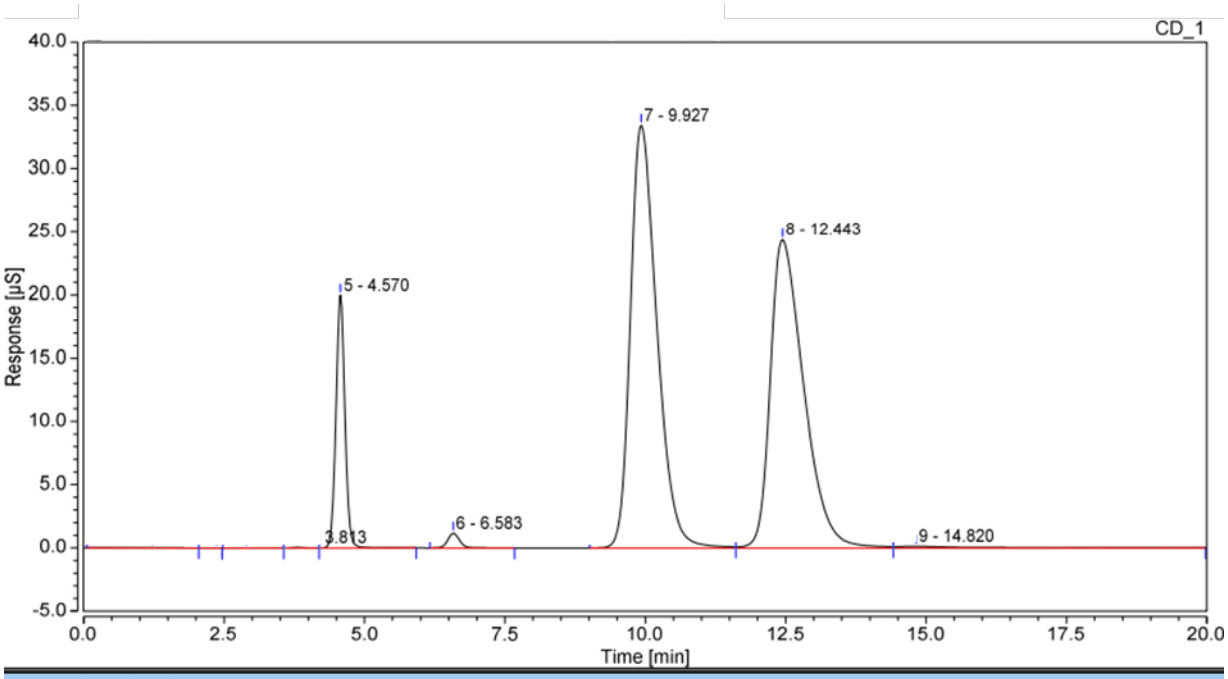
6.1.4 Ion chromatography

The ion chromatography separation column (Dionex IonPac AS11 HC) available at the university was only suitable to separate group 1 and 2 metal ions, thus analysis was focused on the water hardness and ammonium ions rather than transition metal ions (also of interest to the project).

Initial experiments were carried out to establish the retention time of the ions of interest and the construction of calibration graphs. The data was then used to identify peaks in a complex mixture, an example is seen in Figure 6-11.

The data table, seen below the graph, provides detailed information about the detected peaks, including peak height (which is proportional to the concentration and is used in concertation calculations).

All the other peaks are unidentified, the possible ions detected are: potassium or sodium as they are quite common in water samples. However, without separation of known standards it is impossible to determine that. Other peaks were not investigated further in the project.



Integration Results

No.	Peak Name	Retention Time min	Area µS*min	Height µS	Relative Area %	Relative Height %	Amount n.a.
1		1.223	0.026	0.016	0.07	0.02	n.a.
2		2.370	0.010	0.028	0.03	0.03	n.a.
3		2.893	0.023	0.025	0.06	0.03	n.a.
4		3.813	0.015	0.052	0.04	0.07	n.a.
5	NH4	4.570	3.669	20.015	9.35	25.25	n.a.
6		6.583	0.283	1.170	0.72	1.48	n.a.
7	Mg	9.927	18.256	33.454	46.52	42.20	n.a.
8	Ca	12.443	16.787	24.397	42.78	30.77	n.a.
9		14.820	0.177	0.126	0.45	0.16	n.a.
Total:			**39.245**	**79.282**	**100.00**	**100.00**	

Figure 6-11: Example report of IC separation of Highland Spring water sample.

The graph seen in Figure 6-12 present calibration graphs for calcium, magnesium and ammonium ions obtained by plotting data from the ion chromatography separation of samples of known concentration against the detected peak heights. Use of the regression analysis equation allows calculation of the concentration of an unknown sample.

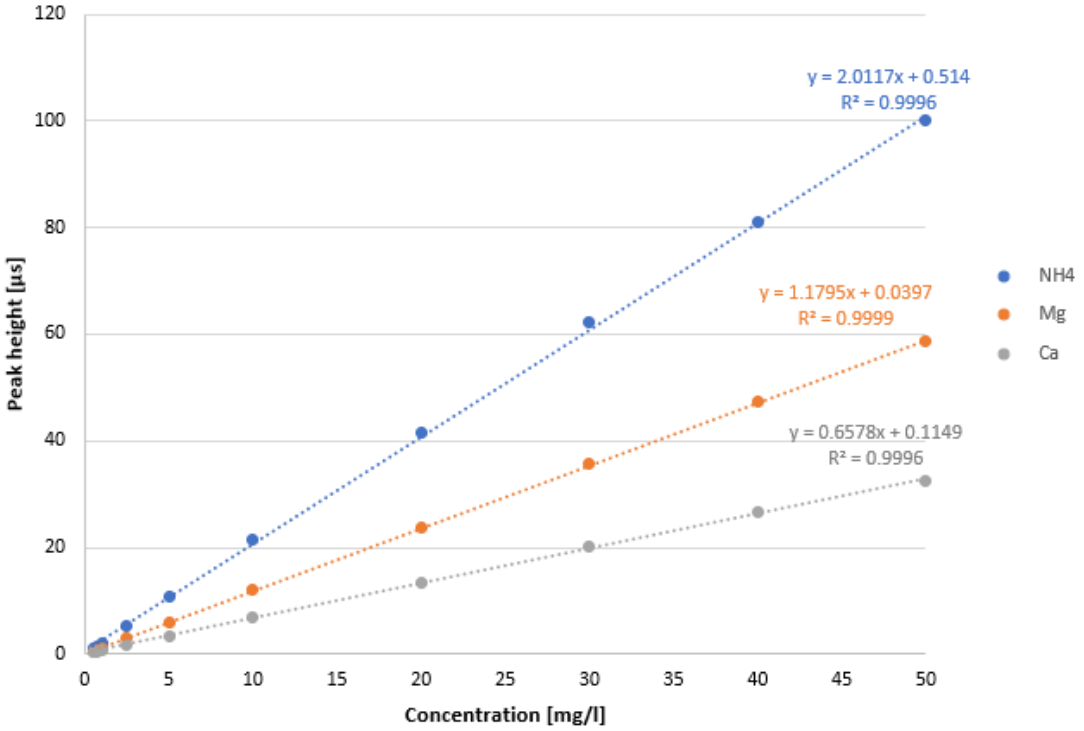


Figure 6-12: Calibration graphs obtained using ion chromatography separation of calcium, magnesium and ammonium ions.

Table 6-8: Summary table for IC separation of calcium, magnesium and ammonium ions.

Ion	Retention time (st dev) [min]	R^2	Concentration [mg/l]	n
Ca^{2+}	12.492 (0.208)	0.9996	0.5-50	10
Mg^{2+}	10.040 (0.078)	0.9999		10
NH_4^+	4.558 (0.022)	0.9996		10

6.1.5 Inductively coupled optical emission spectroscopy (ICP-OES)

All ions were analysed using various wavelengths which provided the best signal. Standards were analysed at the beginning of every experiment and calibration graphs were prepared to calculate the concentrations of the ions. Table 6-9 presents the wavelengths used for calcium and magnesium analysis. Experiments were repeated at least once at each wavelength.

Table 6-9: Wavelength used in calcium and magnesium ions analysis.

Wavelength [nm]	
Ca^{2+}	Mg^{2+}
315.887	202.582
317.933	277.983
318.127	279.078
370.602	279.553
373.690	279.800
393.366	280.270
396.847	283.230
422.673	285.213
430.253	293.651
612.222	383.829
616.217	383.230
643.907	

The concentration of each ion is an average of at least twenty experiments conducted under twelve wavelengths.

6.1.6 **Water softeners**

The number of techniques for water softening is not extensive. The most popular and most effective are the ion-exchange softener, reverse osmosis and lime softening.

6.1.6.1 **Ion exchange water treatment**

During ion exchange, ions responsible for water hardness (Ca^{2+} and Mg^{2+}) are replaced by non-hardness ions (typically Na^{+}) (Figure 6-13). The softener contains a microporous ion exchange resin. When hard water is passed through the resin, calcium and magnesium ions replace sodium ions in the resin. Released sodium ions are in the soft water which is then distributed in the household.
To reactivate the resin, a concentrated solution of NaCl is required. Sodium ions from salt replace calcium and magnesium ions in the resin. The product of that reaction, water rich in hardness-producing salts, is flushed out with wastewater.

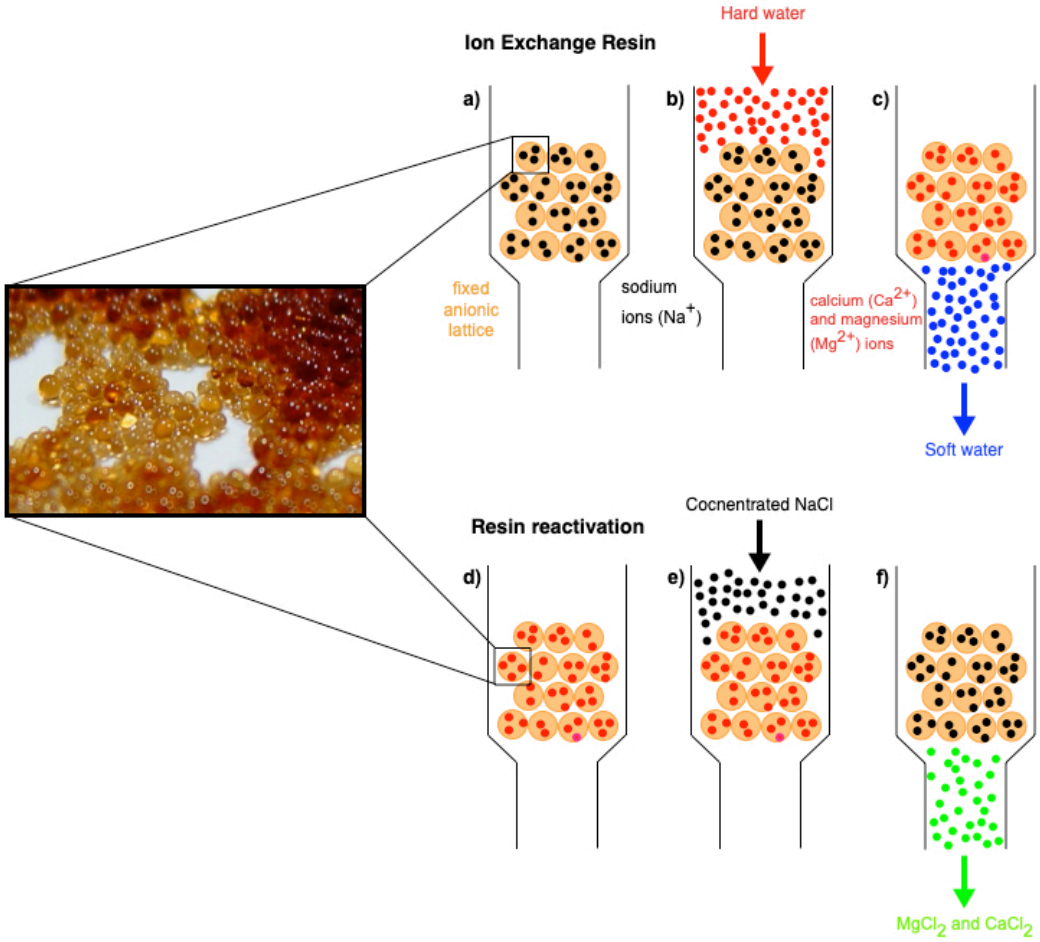


Figure 6-13: Ion exchange resin with the mechanism of exchange a-c) water softening process, d-f) resin reactivation process.

6.1.6.2 **Reverse osmosis**

Osmosis is a natural process where water flows through a membrane from a solution with lower concentration of dissolved ions to a solution with higher concentration, which results in equalisation of the concentration (Figure 6-14a).

In reverse osmosis, which is used in water treatment, water flows from higher to lower concentration. The only way to induce reverse osmosis is to apply pressure to overcome osmotic pressure (Figure 6-14c). Osmotic pressure is defined by the difference in height of the solutions (Figure 6-14b).

The semipermeable membrane allows the flow of water, but stops ions and other larger molecules. The reverse osmosis technique produces pure water free from ions.

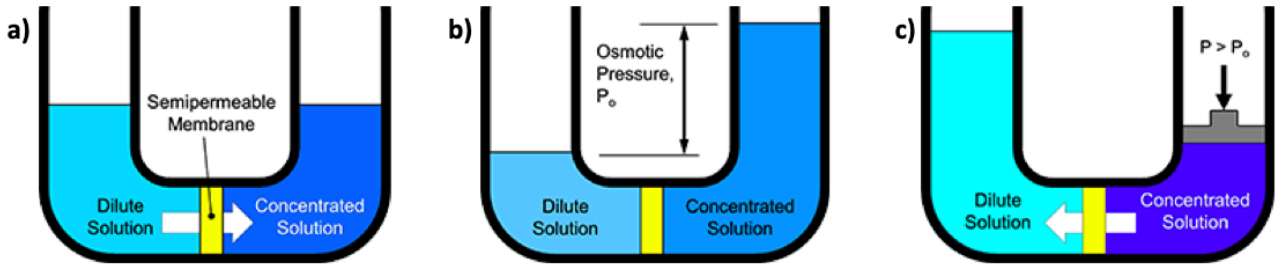


Figure 6-14: Schematic of the osmosis principle. a) osmosis, b) osmotic pressure, c) reverse osmosis.

6.1.6.3 **Lime softening (Clark's process)**

This technique requires the addition of calcium hydroxide and soda ash (Na_2CO_3) to remove the hardness ions (magnesium and calcium) by precipitation (Figure 6-15). In this process the pH of the water must be adjusted to pH 9-9.5 (for magnesium compounds) and to pH 10-10.5 (for calcium compounds).

When lime ($Ca(OH)_2$) is added hardness-causing ions form almost insoluble precipitates ($CaCO_3$, $MgCO_3$ and $Mg(OH)_2$).

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2\,CaCO_3\downarrow + 2\,H_2O$$

$$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow CaCO_3\downarrow + MgCO_3\downarrow + 2\,H_2O$$

$$MgCO_3\downarrow + Ca(OH)_2 \rightarrow CaCO_3\downarrow + Mg(OH)_2\downarrow$$

In the case of the addition of both, lime and soda ash (Na_2CO_3), the process takes slightly less time.

$$MgSO_4 + Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + CaSO_4$$

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3\downarrow + Na_2SO_4$$

The precipitate is removed by coagulation, sedimentation or filtration. However, because the precipitates are very slightly soluble in water, the water hardness in not removed completely. That helps prevention of corrosion problems in pipes in the presence of water that is too soft.

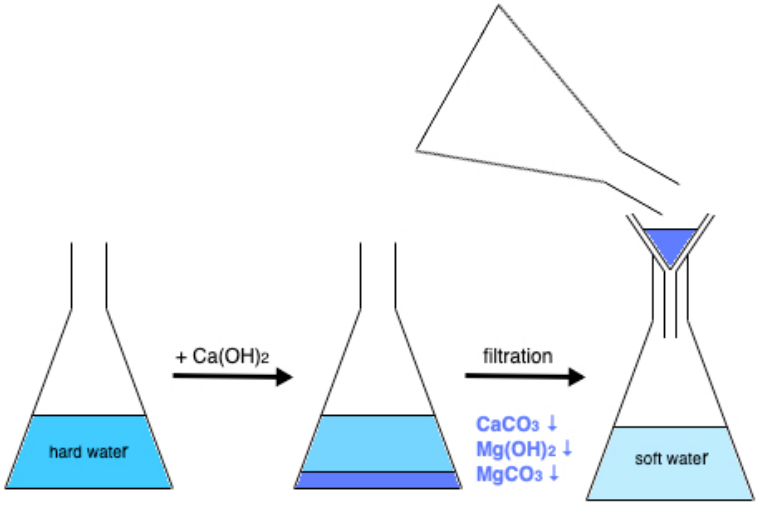


Figure 6-15: Scheme of Clark's process of water treatment.

6.1.6.4 **Chelation technique**

In this technique chelating agents are used as the additive in products used in water, such as: shampoo, soaps or washing liquids. Chelating agents form a stable, water-soluble complex. What has to be noted is that water treated by chelating agents is not suitable for consumption due to high levels of acidity.

Chelating agents have a ring-like centre which forms at least two bonds with the metal ion, they are usually organic compounds. What needs to be noted is that the chelating agents bind not only with calcium and magnesium ions, but with other ions as well (most common are iron, lead or copper ions).

The most popular chelating agents in water industry are presented in Figure 6-16.

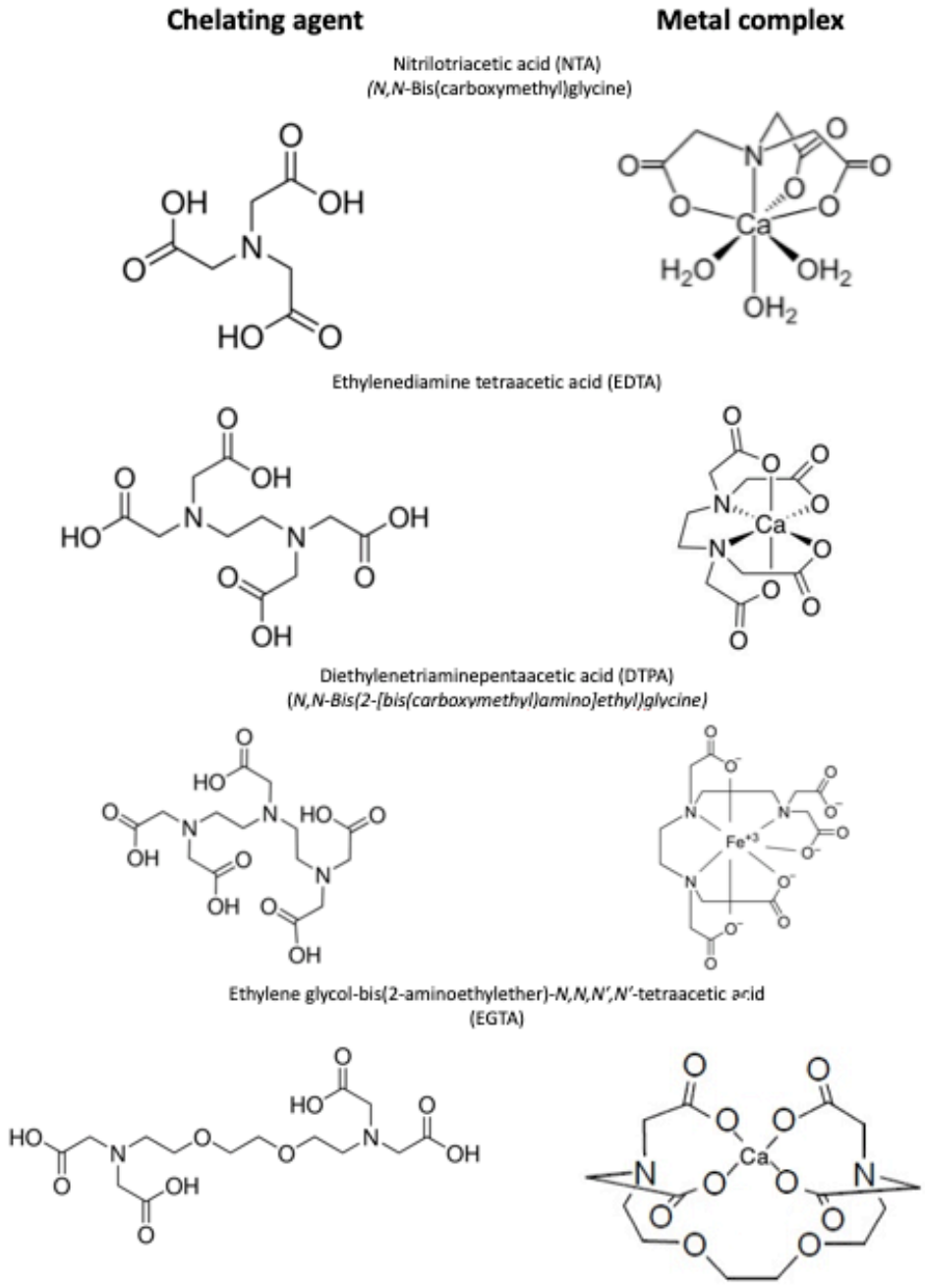


Figure 6-16: Most popular chelating agents in the water industry and their complexes with metal ions.

6.1.6.5 **Boiling of water**

Boiling of water is another technique for softening water, however it is useful only for small quantities. By boiling it is possible to remove some minerals that will settle at the bottom of the solution.

$$Ca(HCO_3)_2 \xrightarrow{boiling\ [°C]} CaCO_3 \downarrow + H_2O + CO_2$$

6.1.6.6 **Adding washing soda**

Washing soda is the common name for sodium carbonate (Na_2CO_3), it can be added to hard water to soften it. Sodium carbonate is soluble in water, carbonate ions react with dissolved calcium and magnesium ions, forming insoluble precipitate.

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + Na_2SO_4$$
$$MgCl_2 + Na_2CO_3 \rightarrow MgCO_3 \downarrow + 2\,NaCl$$

6.2 **Discussion**

Both ions responsible for water hardness were examined using three different techniques.

Table 6-10 and Table 6-11 present the calculated concentrations of calcium and magnesium ions in the samples. Figure 6-17 allows comparison of all the calcium data for each water sample. It is possible to see that there are samples where the obtained concentrations are scattered such as San Pellegrino or Sicily water samples. There are more water samples which present overlapping results – Tesco, Smartwater, Volvic, Sainsbury's, Durham, Stretford, Maybole or B-floor Lancaster University. It is possible to determine that the concentration obtained using various techniques remains fairly constant. In many cases the only odd result is the official data.

Figure 6-18 presents concentrations of magnesium ion in the water samples. The samples which show the most consistent results are: Tesco. Smartwater, Volvic, London, Durham, Stretford, Maybole and B-floor Lancaster University.

It was impossible to obtain information about the techniques and methods, number of samples or the standard deviation of the concentrations used in official data reports. Tap water suppliers only provide annually average data. Thus, it is possible that the official data is different to the actual ion concentrations in the water samples taken within this research programme.

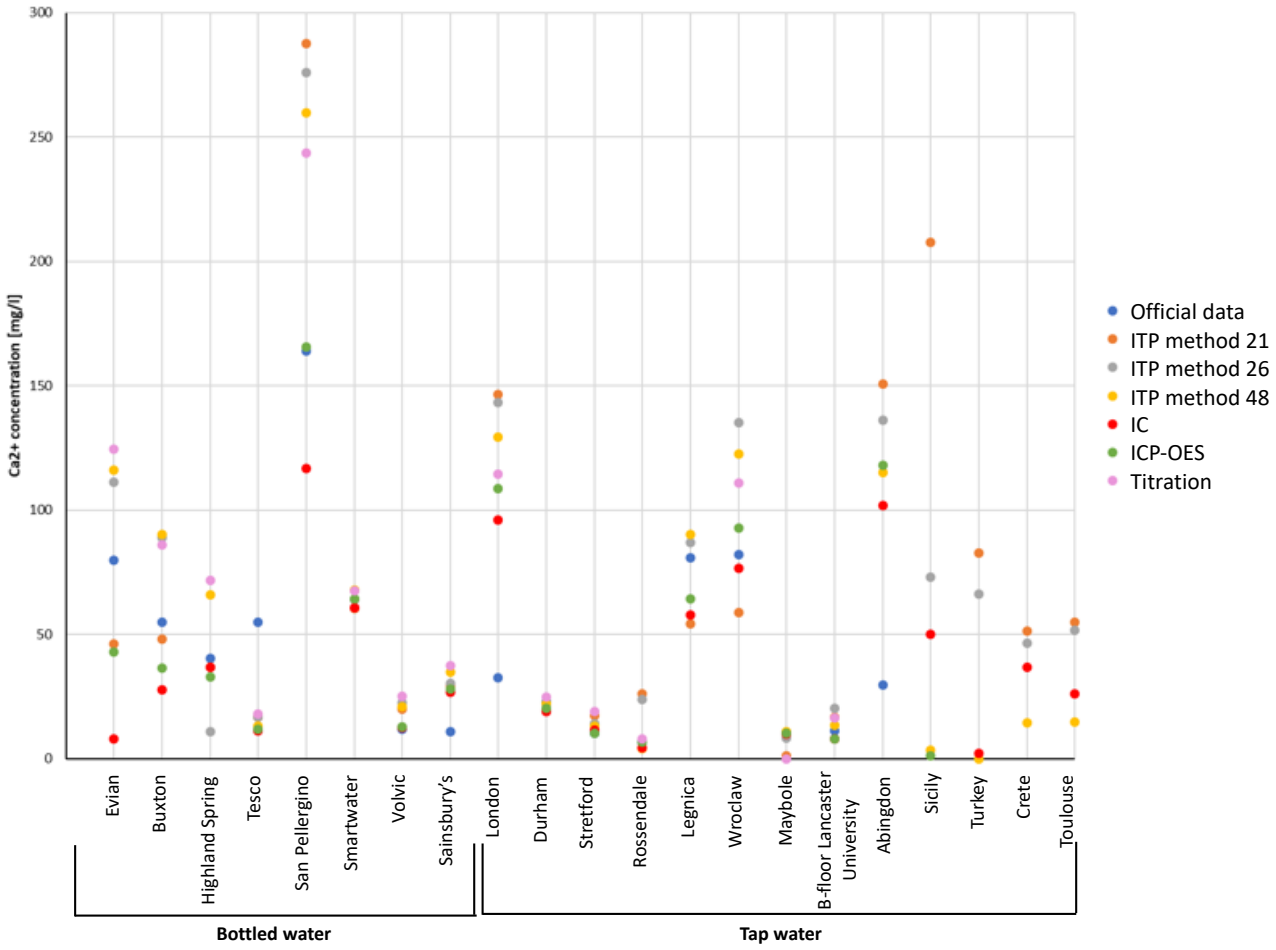


Figure 6-17: Comparison of calcium ion concentration data for water samples.

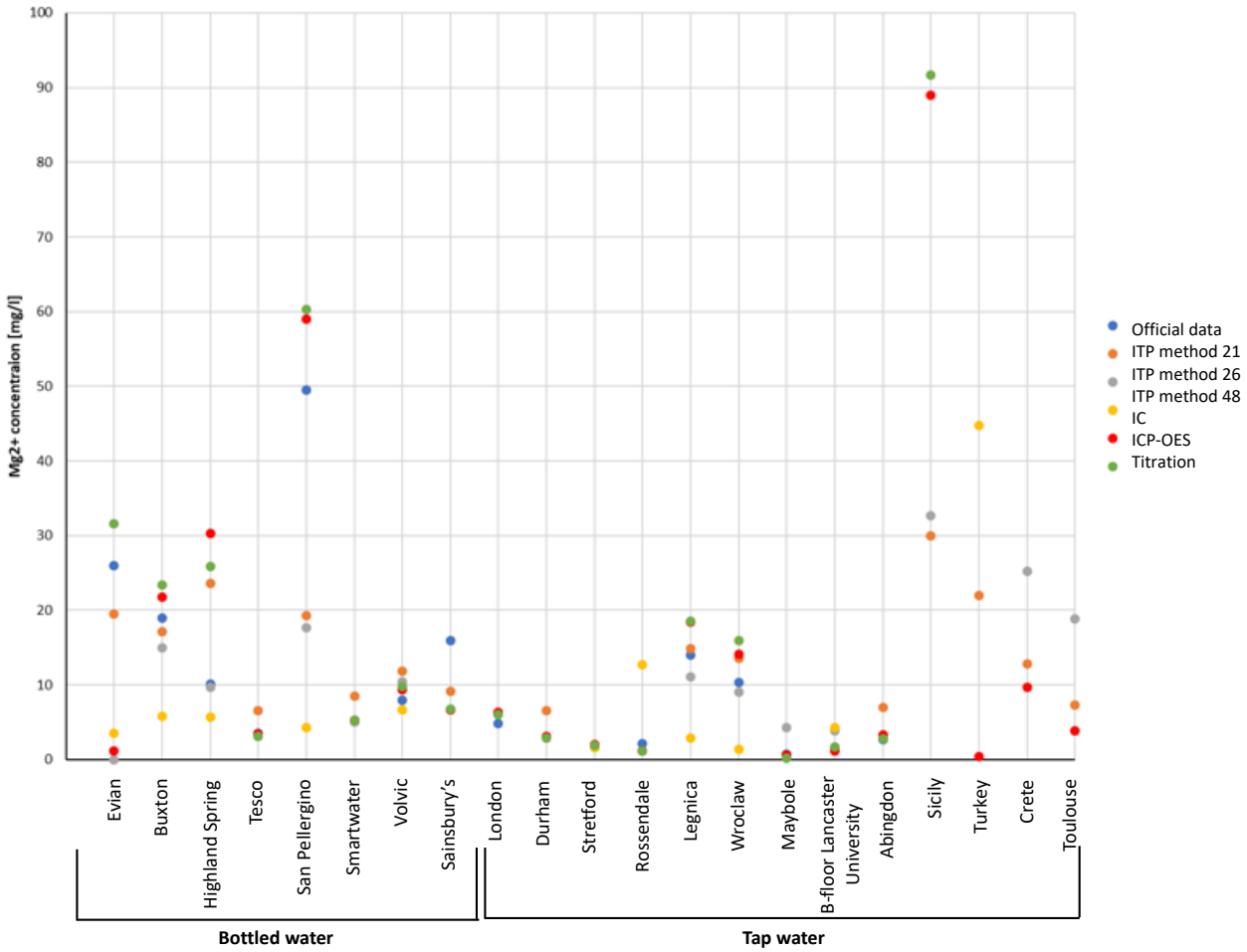


Figure 6-18: Comparison of magnesium ion contractions in water samples.

Table 6-10: Calculated concentrations of Ca^{2+} in real water samples.

Ca^{2+} [mg/l]		Official data	ITP			IC	ICP-OES	Titration
			Method 21	Method 26	Method 48			
Bottled water	Evian	80	46.126	111.290	116.085	7.96	42.98	124.48
	Buxton	55	48.249	89.071	90.308	27.71	36.38	85.98
	Highland Spring	40.5	36.926	11.025	66.055	36.77	33.12	71.74
	Tesco	55	16.730	16.654	13.242	11.44	11.82	17.94
	San Pellegrino	164	287.723	275.975	259.88	116.64	165.82	243.68
	Smartwater	N\A	60.515	64.132	67.875	60.68	64.37	67.52
	Volvic	12	19.96	22.751	21.129	12.44	12.79	25.32
	Sainsbury's	11	29.414	30.271	34.804	26.66	27.96	37.46
Tap water	London	32.8	146.58	143.197	129.494	95.93	108.64	114.46
	Durham	23	20.033	21.901	22.351	19.15	20.19	24.80
	Stretford	10.4	17.293	14.105	13.067	11.58	10.35	19.00
	Rossendale	6.88	26.021	23.962	4.297	4.40	6.76	7.92
	Legnica	81	54.183	87.010	90.139	57.93	64.26	—
	Wroclaw	82.2	58.876	135.316	122.756	76.70	92.79	111.03
	Maybole	10.78	1.379	8.412	11.071	9.95	10.35	—
	B-floor	11.3	16.658	20.435	13.678	7.91	8.02	16.36
	Abingdon	29.7	150.745	136.154	115.104	101.89	118.11	—
	Sicily	N\A	207.745	73.155	3.569	50.08	1.31	—
	Turkey	N\A	82.954	66.385	—	2.32	—	—
	Crete	N\A	51.325	46.428	14.652	36.78	—	—
	Toulouse	N\A	55.127	51.781	14.957	26.26	—	—

Table 6-11: Calculated concentrations of Mg^{2+} in real water samples.

Mg^{2+} [mg/l]		Official data	ITP			IC	ICP-OES
			Method 21	Method 26	Method 48		
Bottled water	Evian	26	19.564	Not det	3.526	1.22	31.63
	Buxton	19	17.104	14.940	5.802	21.80	23.37
	Highland Spring	10.10	23.582	9.746	5.720	30.32	25.87
	Tesco	3.50	6.558	Not det	3.312	3.46	3.10
	San Pellegrino	49.50	19.321	17.626	4.318	58.98	60.25
	Smartwater	N/A	8.502	5.070	—	5.26	5.31
	Volvic	8	11.821	10.453	6.648	9.41	9.79
	Sainsbury's	16	9.139	6.637	—	6.64	6.83
Tap water	London	4.85	6.194	Not det	—	6.31	6.07
	Durham	N\A	6.558	Not det	—	3.11	2.86
	Stretford	1.76	Not det	Not det	1.596	2.07	1.97
	Rossendale	2.16	Not det	Not det	12.685	1.21	1.16
	Legnica	14	14.847	11.089	2.866	18.39	18.49
	Wroclaw	10.3	13.617	9.016	1.341	14.07	15.97
	Maybole	0.73	Not det	4.293	—	0.66	0.20
	B-floor	1.52	Not det	3.881	4.260	1.22	1.68
	Abingdon	2.65	7.001	Not det	—	3.30	2.84
	Sicily	N\A	30.011	32.723	—	88.99	91.65
	Turkey	N\A	22.031	Not det	44.708	0.42	—
	Crete	N\A	12.838	25.254	—	9.65	—
	Toulouse	N\A	7.318	18.812	—	3.85	—

Chapter 7 Metal ions and ammonium ion

7.1 **Isotachophoresis**

Isotachophoresis is a perfect technique to analyse specific oxidation states of transition metal ions. It allows recognition of iron (II) and iron (III), chromium (III) and chromium (VI).

Number of electrolyte systems were investigated in the project to detect metal ions. The project focused on: lead, iron (II), chromium (III), aluminium and copper ions.
Table 7-1 presents all calibration data obtained from ions analysis. As seen in the table, various range of concentrations were analysed to prepare the calibration graphs.

Relative step heights and their standard deviation were calculated based on all samples (*n*). considering that the biggest deviation is at 0.023, it is possible to conclude that isotachophoresis gives consistent results through the wide range of samples and concentrations.
R^2 values provides additional information about how powerful technique is the ITP. Only one calibration graph had R^2 value lower than 0.99, it was separation of lead using Method 85 with R^2 of 0.9887.
Equation presented in the table are obtained from the calibration graphs and can be used to calculate the ion concentration of the sample. The choice of the lowest concentration was experimentally chosen. Multiple analysis at each concentration was performed to provide sufficient data to prove the consistency of separation conditions.

There were no ammonium or metal ions detected in the samples.

Table 7-1: Summary of calibrations conducted for metals and ammonium ions.

Ion	Method	pH	RSH (st dev)	R^2	Equation	Concentration [mg/l]	n
NH_4^+	21	9.0	0.355 (0.008)	0.9968	x=(y+0.128)/1.2672	5-100	66
	48	2.0	0.268 (0.005)	0.9990	x=(y-7.7748)/3.1884	0.25-50	30
	57	2.0	0.263 (0.004)	0.9992	x=(y-2.3899)/2.0265	0.25-100	90
Al^{3+}	13	4.1	0.994 (0.005)	0.9990	x=(y+1.2454)/0.9286	2.5-100	36
	48	2.0	0.422 (0.021)	0.9992	x=(y+30.303)/6.7147	5-50	18
Cr^{3+}	4	4.9	0.138 (0.002)	0.9985	x=(y+4.704)/0.5661	20-50	12
	5	4.9	0.247 (0.002)	0.9944	x=(y+6.0964)/0.8668	10-100	30
	48	2.0	0.583 (0.006)	0.9988	x=(y+12.832)/2.5705	5-50	18
Cu^{2+}	4	4.9	0.446 (0.006)	0.9979	x=(y+0.0584)/0.7894	5-100	33
	12	4.9	0.484 (0.023)	0.9981	x=(y+2.6052)/0.2913	20-100	27
	26	4.8	0.574 (0.005)	0.9998	x=(y-1.842)/0.3911	20-50	12
	48	2.0	0.456 (0.007)	0.9995	x=(y+0.4942)/2.0858	1-50	26
Fe^{2+}	4	4.9	0.065 (0.002)	0.9935	x=(y+2.5367)/0.9999	10-50	15
	5	4.9	0.290 (0.007)	0.9986	x=(y+0.8544)/0.7993	5-100	33
	48	2.0	0.465 (0.008)	0.9969	x=(y-2.4678)/2.4351	0.5-50	28
Pb^{2+}	4	4.9	0.200 (0.002)	0.9997	x=(y+0.7389)/2.2836	5-50	18
	26	4.8	0.298 (0.003)	0.9970	x=(y+3.1599)/1.6841	5-50	18
	48	2.0	0.454 (0.004)	0.9968	x=(y-5.27)/5.5487	1-50	24
	85	4.7	0.311 (0.006)	0.9887	x=(y+3.912)/0.357	10-100	30

7.2 **Inductively couple plasma – optical emission spectroscopy**

Various wavelengths were used in analysis of the elements as seen in Table 4-1. Multiple runs were done for the samples, in most of the cases the elements were not detected or were detected only in few runs. Thus, the data is not reliable and should be treated only as an estimate. Considering that the concentrations of metal ions are expected to be low in the samples, as seen in Table 5-4, the data is as expected (Table 7-2). To improve the results standards with lower concentrations should be lower than the analysed in this project (<0.25mg/l).

Table 7-2: ICP-OES results of samples analysis.

	Element analysed	Al	Cr	Cu	Fe	Pb
Bottled water	Evian	—	0.23	—	0.02	0.20
	Buxton	0.32	0.02	0.38	0.18	0.11
	Highland Spring	0.69	0.00	1.74	0.00	0.15
	Tesco	0.42	0.00	—	0.02	0.22
	San Pellegrino	—	0.44	—	0.10	0.06
	Smartwater	0.53	0.01	—	0.10	0.09
	Volvic	—	—	—	0.09	0.16
	Sainsbury's	—	0.04	0.58	0.01	0.52
Tap water	London	—	—	0.05	—	0.07
	Durham	0.46	0.00	—	0.18	0.56
	Stretford	0.12	—	—	0.04	0.10
	Rossendale	0.19	0.01	0.77	0.04	0.12
	Legnica	0.08	—	0.03	0.28	—
	Wroclaw	0.07	0.17	—	0.01	0.15
	Maybole	0.15	—	—	—	0.10
	B-floor Lancaster University	—	0.27	—	0.04	0.13
	Abingdon	—	—	—	—	—
	Sicily	—	—	—	—	—
	Turkey	—	—	—	—	—

Chapter 8 Construction of the water monitor prototype, based on ITP

The prototype consists of a power supply, electrolytes and sample injection system, separation tubbing, detector and data logger.

8.1 Interlock and safety box

As a safety precaution while working with the high voltage, a safety box with an interlock was used. The power would get cut off in case the door becomes open, whereby the interlock disconnected the high voltage source (via a rapid action high voltage relay) and power supply to the high voltage generator.

The box was made of Perspex with dimensions of 62.5x41.5x35.5cm (LxHxW). All the components of the separation system were placed in the safety box. Figure 8-1 and Figure 8-2 presents top and side views.

Figure 8-1: Instrument prototype in the safety box side view.

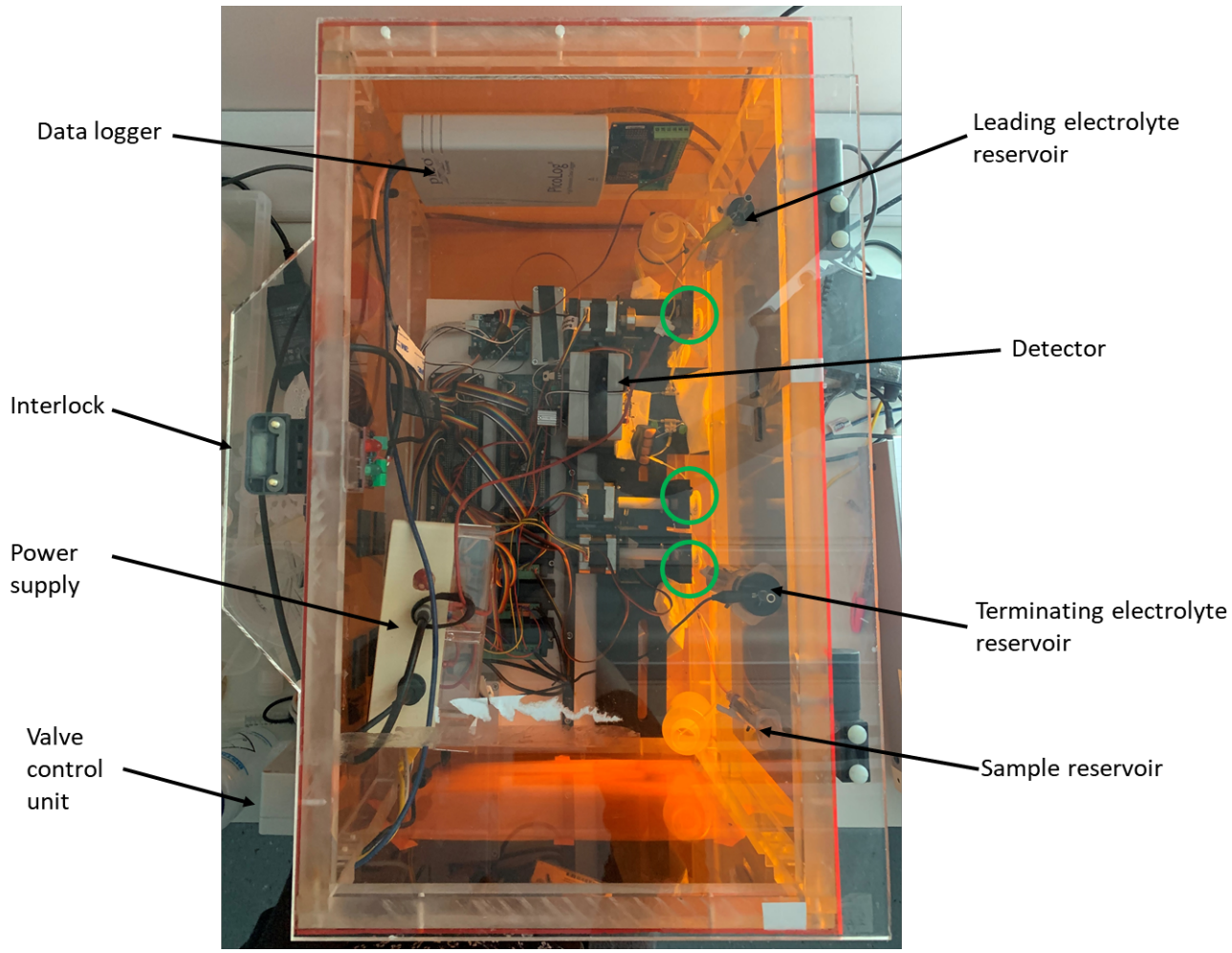


Figure 8-2: The main components of the instrument prototype in the safety box (top view), marked in green are the valves.

8.2 **Electrolytes solutions and electrodes**

Syringe barrels were used as electrolytes reservoirs. There were connected to the ITP separation system by stopcocks which allow opening of the flow while filling the electrolyte and running the separation.

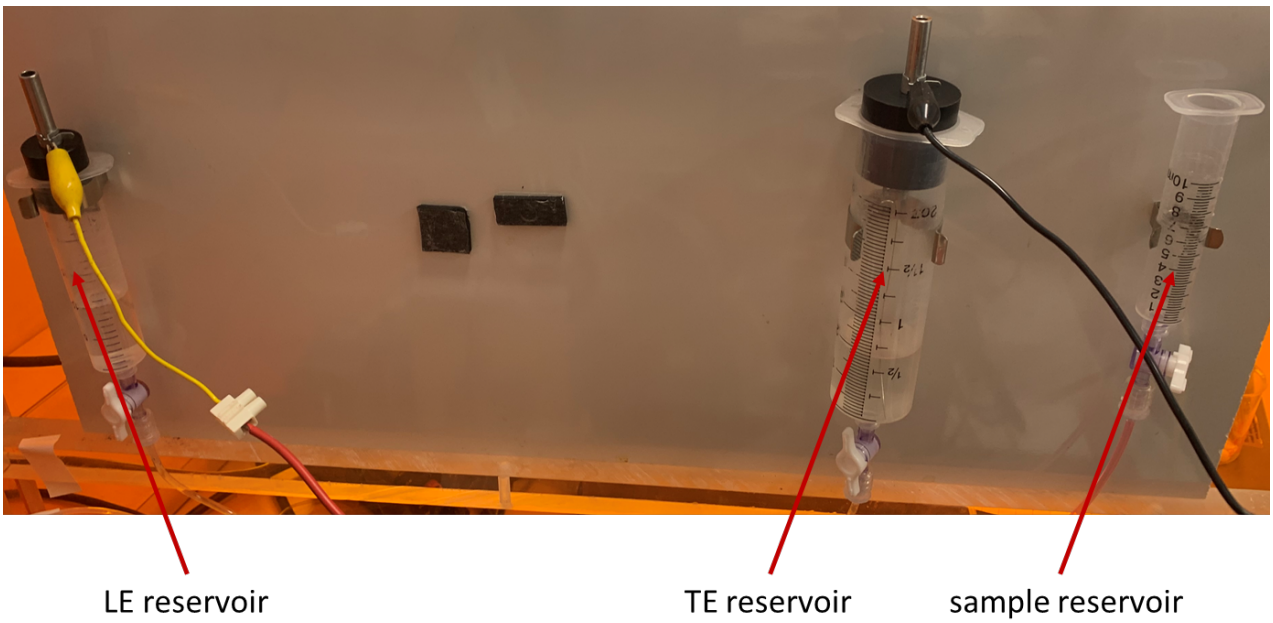


Figure 8-3: Electrolytes and sample reservoirs.

The SRS power supply outlet cables were connected to the platinum wire (platinum wire, diam. 0.5mm, 99.9%, Aldrich) immersed in the electrolytes' solutions (Figure 8-4).

During any electro separation process the gas bubbles can form on the electrode (Figure 8-4b). Accumulation of the gas bubbles in the separation system resulted in the drop of the current and in the worse scenarios prevented the separation. In the case where many gas bubbles obstructed the tubing, even sparks were observed. Hence a stainless steel tube, where the HV is connected is an empty tube, so the gas can escape, was used as a method to reduce accumulation of gas bubbles and their injection into the separation system.

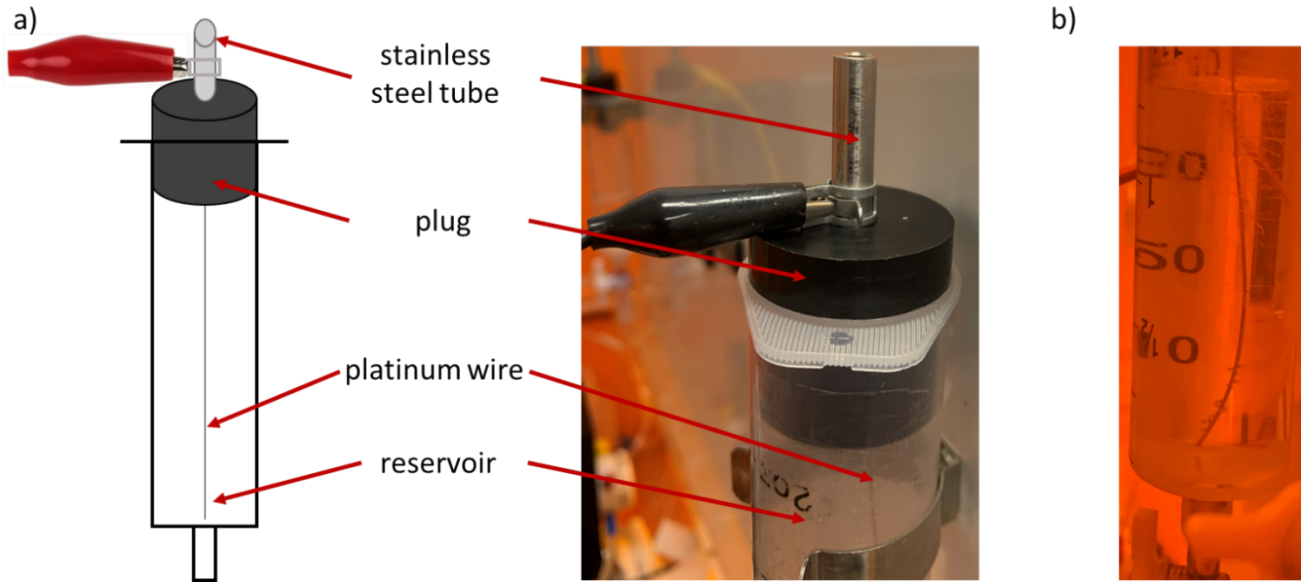


Figure 8-4: a) setup of the electrolyte reservoirs (syringes), b) gas bubbles formed on the electrode.

8.3 **PicoLog data logger**

A PicoLog data logger (ADC-24) was used to record the data. It provides 24-bit resolution and is able to detect small signal changes. A user can connect up to 16 single-ended inputs, the logger software is easy to use and allows collection, analysis and manipulation of data.

The data logger is connected to the computer and the logged data is plotted on the graph.

Figure 8-5: PicoLog data logger used during the experiments.

8.4 **Power supply**

The power supply used in the prototype setup was Stanford Research System Inc Model PS350 (Figure 8-6). The maximum voltage is 5,000V, the polarity can be changed so separation and hence detection of both cations or anions is possible. Unfortunately, this power supply could not be run satisfactorily in constant current mode.

Figure 8-6: Stanford Research System power supply used in the project.

The sponsoring company had designed and constructed a bespoke high voltage supply for this prototype, which should have been able to provide both constant voltage and constant current modes of operation. Additional safety elements had been designed in, such as being able to set maximum voltages and currents. A safety overload cut-off was also a design feature. Unfortunately, it was unreliable (mainly through failure of the USB interface) and unusable for the duration of a separation. The company had to furlough it development team during Covid-19 pandemic, which made it impossible to have the high voltage power supply operational during this PhD programme. This was a very significant problem that stunted the progress with the prototype ITP system. The rest of the prototype was assembled without input from the sponsors, which was also a significant deficiency in the final part of the PhD programme, as valuable time was spent building the prototype rather than gathering vital separation data. The high voltage power supply was the most significant issue, as the project could not easily use a constant current mode of separation, which is the normal mode used in analytical ITP.

8.5 **Detector**

Essential to the successful realisation of a working at-line ITP instrument, is the design of a robust conductivity detector that will offer sufficient sensitivity to be able to recognise the small changes in conductivity associated with a typical ITP separation. Typically ITP conductivity detectors may be defined by their sensing electrodes as either “contacting” or “contactless”. The advantage of a contactless detector is that there is no direct DC contact with the ITP electrolytes, and therefore no circuit link into the high voltages that are used to drive an ITP separation. However, contactless

detectors are usually based upon the induction of radio-frequencies into the electrolyte by two pairs of electrodes. Generally, the additional electrodes and the slightly remote nature of the electrode geometry results in a reduced spatial resolution of the ITP separation. This means that even if a sharp boundary has been formed by the ITP separation mechanism within the analytical separation tube, the detector will not reproduce the sharpness of the boundary as the contactless detection zone may be more than a millimetre in length, compared to the ITP separation boundary that may be as narrow as 50μm.

The advantage of a contacting ITP conductivity detector is that the electrode geometry may be constructed easily to be as small as 0.5mm, thus offering a superior spatial resolution to that associated with a contactless detector design. Furthermore, the introduction of high (radio) frequencies in the detection process may yield unwanted stray electrical fields in an industrial environment.

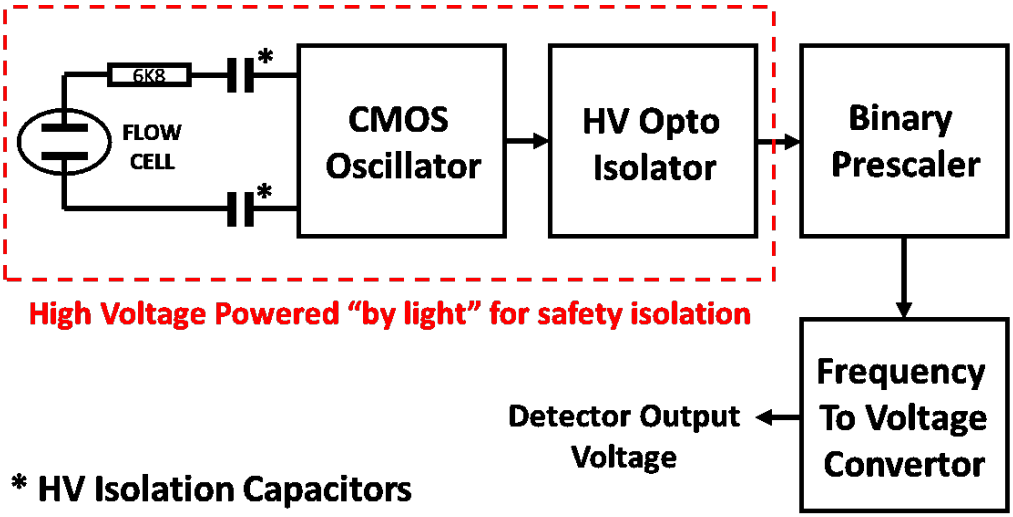


Figure 8-7: A schematic of the prototype conductivity detection circuit with high voltage isolation.

Figure 8-7 shows the essential elements of the conductivity detector. At the heart is a flow cell that is compatible with the dimensions of the ITP separation capillary. The detection cell uses a parallel opposing pair of 0.5mm diameter platinum wires, spaced at 0.5mm across the direction of the ITP separation. The pair of contacting electrodes are separated from a digital oscillator by high voltage isolation capacitors (C*, in the figure). A serial resistor (6k8Ω) has been added to assisting the linearisation of the detector response to conductivity[63]. The isolation capacitors are required to be as high a value as is practicable, and is this design are formed from a parallel pair of 0.001μF disc-

ceramic capacitors rated at 15kV (Farnell Ltd., 1000pF, 15kV, 20%, Y5U), which yields an isolation capacitor of 0.002µF. The oscillator uses 4000 series CMOS invertors, as detailed in a previous publicationva[63]. The frequency output of the oscillator is further isolated by feeding the output via an opto-isolator, rated at 5kV (PC817). The entire 5V DC power supply used to feed the oscillator and opto-isolator input stage is generated through the illumination of a 4.5V photocell with an array of LEDs contained within a plastic (ABS) box, where the spacing between the LED array and the photocell is 5cm. This section of the circuit is therefore fully isolated from the rest of the detection circuitry to at least the specified breakdown voltage of the opto-isolator (5kV), but with the additional protection through the 15kV isolation capacitors.

A switch-selectable binary pre-scaler has been added to divide the oscillator output frequency in multiples of two. A CD4040 12-stage Ripple-Carry binary counter/divider was employed, with only seven of the twelve stages used. The purpose of the pre-scaler is to optimise the detection sensitivity range, and to frequency match the final frequency-to-voltage convertor. This was typically operated as a divide by eight unit for the data reported from the prototype. The output voltage was followed and logged by a commercial data-logger (section 8.3).

8.5.1 **Flow cell**

The flow cell design was based upon the design reported previously[63] and shown in Figure 8-8.

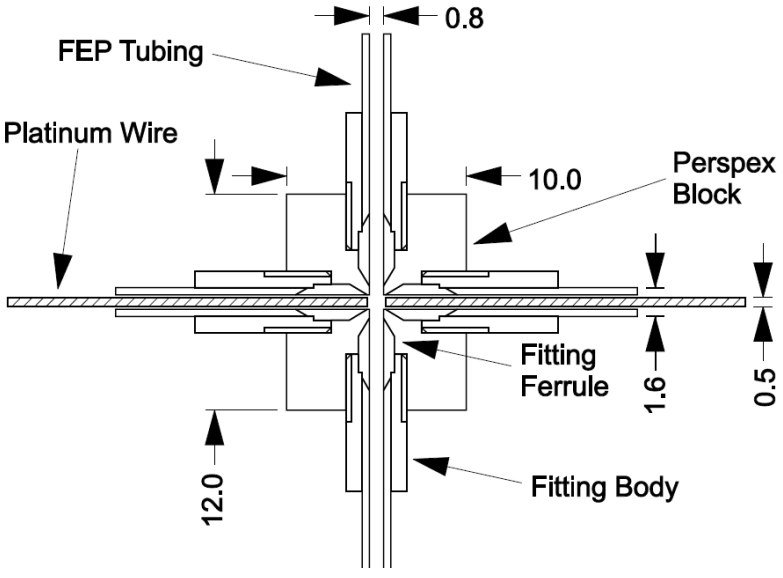


Figure 8-8: Drawing to show design concept for the contacting conductivity detector flow cell[63].

The flow cell uses 1/16” OD commercial connectors (062 MINSTAC® System; The Lee Company, Ltd., CT, USA) to form a leak-tight seal between the input and output capillary tubes, and the platinum electrodes sealed within 1/16” OD, 0.5mm ID FEP tubing, that is similarly compatible with the 062 MINSTAC® System connectors. The flow cell is therefore minimal in terms of the disturbance of the flow path geometry. The prototype flow cell used within this project was similar to this reported flow cell, but for convenience used commercial connectors (as were available to the project), rather than a bespoke machined Perspex block (which was no longer available). Instead, the detector electrodes were mounted in a five-way connector and joined to a three-way connector. The geometries of these commercial connectors are shown in Figure 8-9.

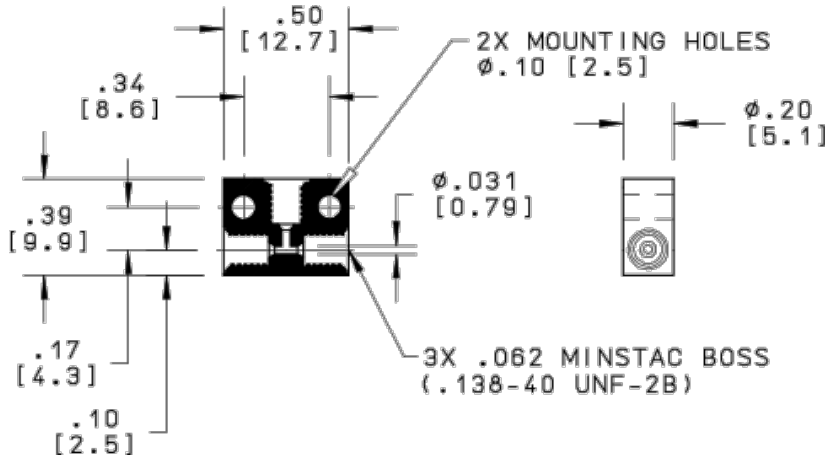


Figure 8-9: Schematics of the two commercial 062 MINSTAC® System junction manifolds used to form the prototype flow cell. Left is the five-way junction manifold, and right is the three-way junction manifold[64].

The junction manifolds shown in Figure 8-9 were configured as shown in the flow-cell schematic in Figure 8-10.

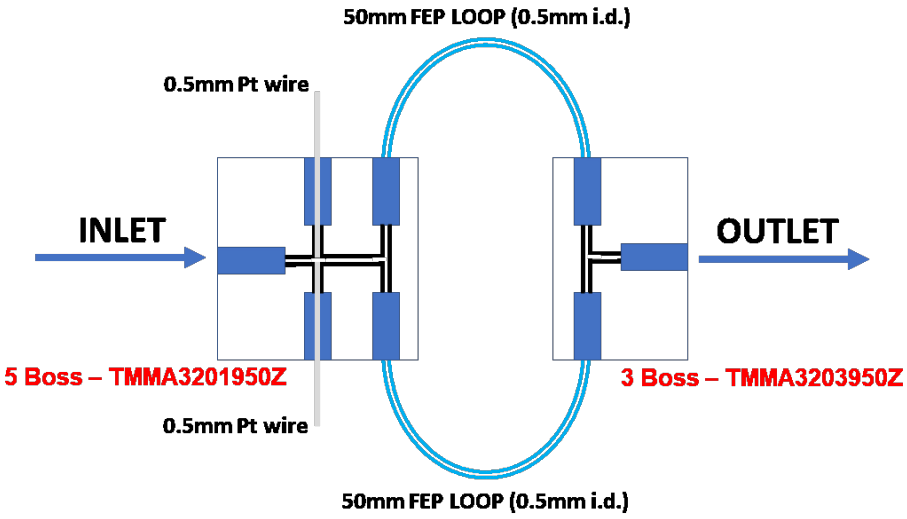


Figure 8-10: Schematic to show how the commercial 062 MINSTAC® System three and five-way junction manifolds were joined for the detector flow cell in the ITP prototype instrument.

The arrangement in Figure 8-10 was undertaken as a matter of pragmatism. Ideally, a four-way cross junction manifold should be used. However, as only a five-way and three-way junction were available, these were joined as shown in Figure 8-10. Since the outlet requires the additional 50mm lengths of FEP tubing, this has the disadvantage of increasing the overall length of the separation manifold. In practical terms, this requires a higher separation drive voltage than a shorter manifold, had the four-way cross connector been available. However, in terms of detection resolution, this design had no detrimental impact since the detection process occurs close to the input of the five-way junction manifold.

8.5.2 **Frequency to voltage convertor**

The output frequency, after pre-scaling, is changed to a linear voltage output since the data-logger requires a signal voltage input. The frequency-to-voltage convertor was based around a LM2917-N14 (Texas Instruments, Inc., Dallas, USA) frequency-to-voltage convertor “chip” which is frequently used in commercial tachometer circuits. For the application to convert the output frequency of the detection oscillator, this device is ideal as it may be configured to provide a linear frequency-to-voltage transfer function over a wide range, and up to 0-100kHz. Figure 8-11 shows a typical application circuit for this device, and the specific component choices made for the needs of the prototype detector.

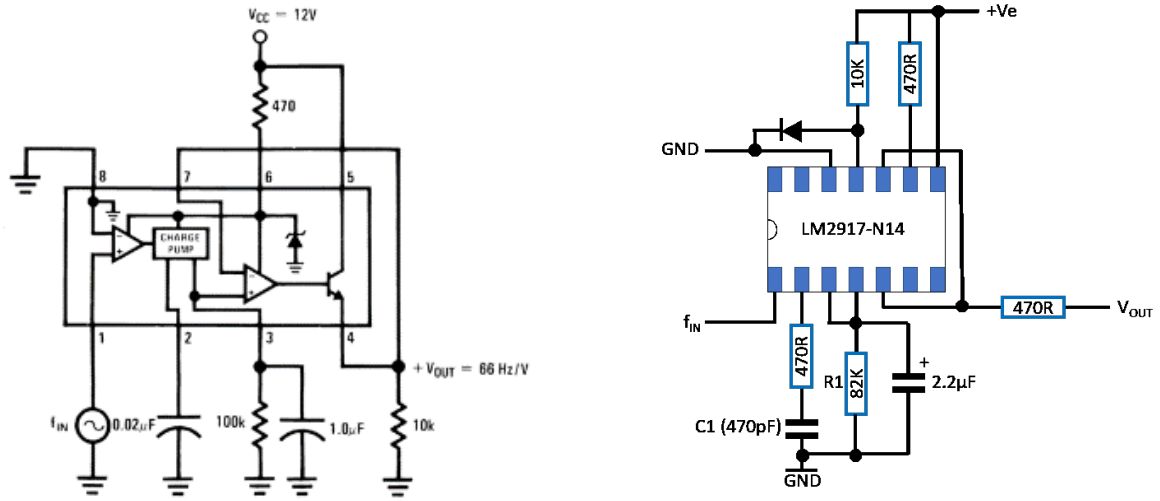


Figure 8-11: A schematic of a typical tachometer application circuit for the LM2917-N14[65] (left); and the actual circuit components and configuration for the detector prototype to yield an output of 1V per kHz (right).

8.5.3 **Detector evaluation**

Once assembled, the high-voltage isolated contacting conductivity detector prototype was evaluated for its response to solutions of potassium chloride at a series of standard concentrations. Figure 8-12 and Table 8-1 show how the detector output response varies with potassium chloride standard solution concentration.

Table 8-1: Results of the detector calibration using KCl solutions at various concentrations.

	KCl concentration [M]			
Voltage [V]	**0.1**	**0.05**	**0.01**	**0.05**
100	8.8	7	2	0.9
200	20.5	16	4	1.7
300	33	25	7.5	2.7
400	46	34	11	3.6
500	60	44	15	5.2
600	73	52	19	6.5
700	80	62	23	7.5
800	85	73	28	9
900	94	80	34	10.5
1000	98	84	39	12.5

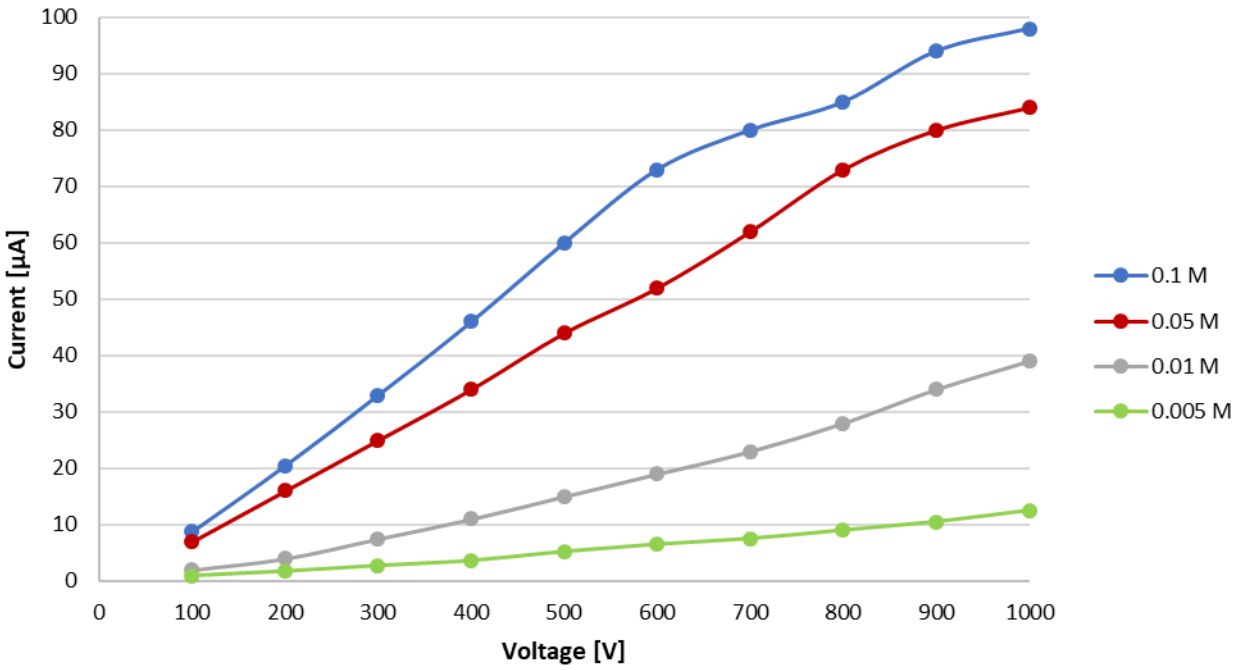


Figure 8-12: Graph to show the detector output as a function of KCl standard solution concentration calibration within the flow cell (laboratory temperature is ca, 20°C).

It is clear from the calibration curve in Figure 8-12, that over the range of $5x10^{-5}$M to 1.0M potassium chloride, the detector response in distinctly non-linear. However, most of the ITP separation process occurs at the lower end of the conductivity range, where the response approximates to linear more closely. It is unlikely that electrolytes at a concentration of 1M will be used in any practical separation. Table 8-2 shows the "raw" frequency output of the detector oscillator for a variety of electrolyte solution, that are more typical of the leading and terminating electrolyte solutions used in practical ITP separations over the sample concentration ranges required.

Table 8-2: A table that shows the frequency output of the detector oscillator for a number of typical electrolyte solutions employed in ITP separations. Water is added for comparison as essentially the baseline conductivity.

Sample Solution/Electrolyte	Oscillator Frequency [Hz]
DI Water	33000
TE 10mM TRIS	32765
TE 10mM BTP	32750
TE 10mM Car. Hydro.	28960
TE 10mM TBA	27917
LE 20mM NH4OH; 10mM HIBA; 0.2% HPC	29775
LE 10mM NaOH; 5mM HIBA; 0.1% HEC	29004
LE 10mM CsOH	27078
LE 10mM HCl; 0,05% Mowiol	25210

8.5.4 **Cell constant**

Most conductivity detector cells are characterised by their "cell constant". The relationship between the cell constant and conductance, G, (siemens, S, or Ω^{-1}) is given by equation 19[66]:

$$\frac{1}{G} = \frac{\rho l}{A} = \frac{l}{\kappa A} \qquad \text{(Eq 19)}$$

Where ρ is specific resistivity [Ωm]

κ is specific (or electrolyte) conductivity [$\Omega^{-1}m^{-1}$] or [S m^{-1}].

The "cell constant" is represented by l/A, which is why the conductance is shown in reciprocal form. Since the area of the platinum wire electrodes in the flow cell are 0.5mm in diameter, the area, A is given as πr^2. Such that the area is: 1.96 x 10^{-7} m^2. And l, the length between the electrodes, is 5 x 10^{-4} m. The cell constant is usually represented by lower-case K (not to be confused with "kappa", the symbol used for specific conductivity). So, equation 20 provides the cell constant for the prototype flow cell, based upon the intended geometry:

$$K = l/A = 5 \times 10^{-4}\ m / 1.96 \times 10^{-7}\ m^2 = \underline{2546\ m^{-1}} \qquad \text{(Eq 20)}$$

This value for the cell constant compares favourably with the measured cell constant reported in the research group's earlier publication[63] of 2615 m^{-1}.

8.6 **Separation system**

The system consists of three Omnifit 3-way valves (Figure 8-13). These are connected via the PTFE tubbing.

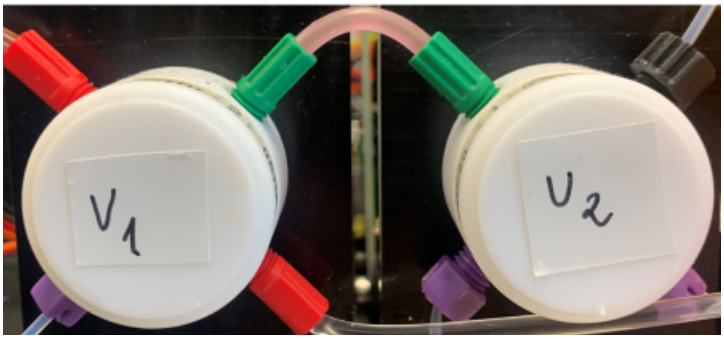


Figure 8-13: Valves used in the prototype.

To be able to control position of the valves using the control panel (Figure 8-17) the start point of the valves must remain constant. To obtain that the optical detector was installed. It consists of the plastic slit where the light detector is placed. The valve is connected to the motor by the PTFE sleeve, where a screw is situated. When the valve is moving so is the Teflon sleeve and the screw. When the valve is commanded to go to its 'start position' the valve starts moving in the clockwise direction (Figure 8-14a) until the screw cuts through the light (Figure 8-14b). Then it turns an additional 1/8 turn to reach the start position (Figure 8-14c).

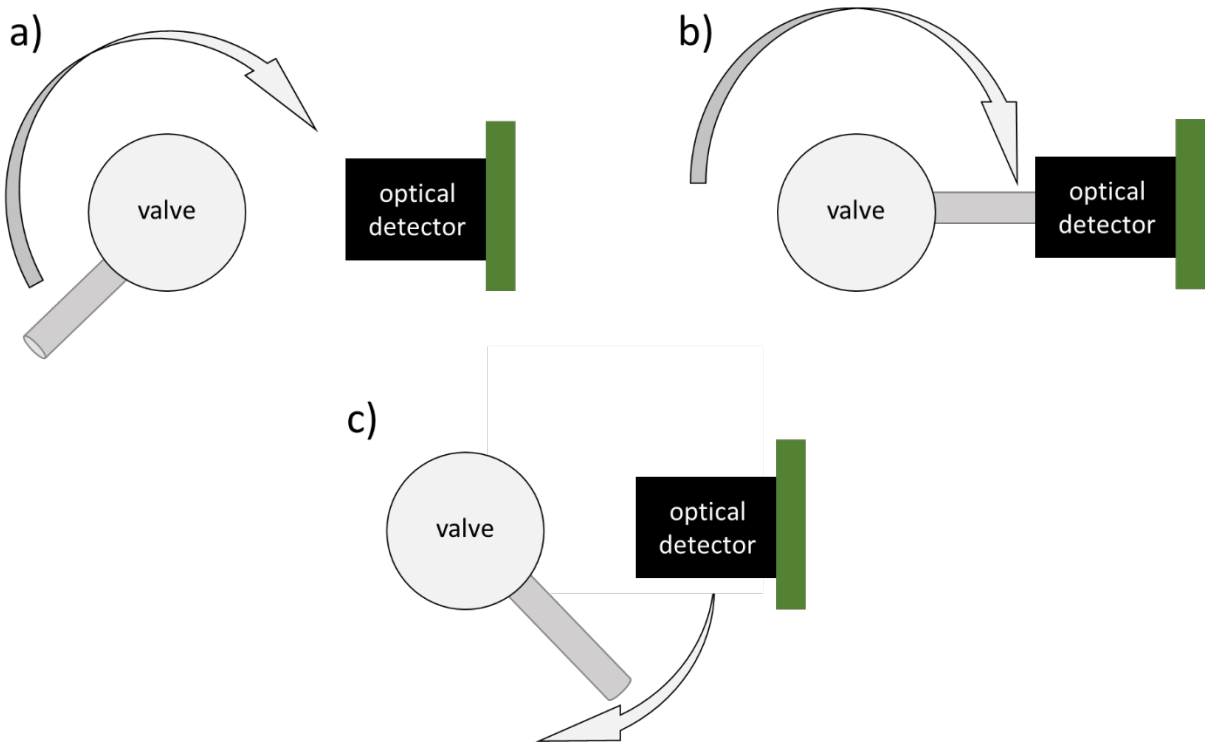


Figure 8-14: Operation of the optical detector used to position the valve.

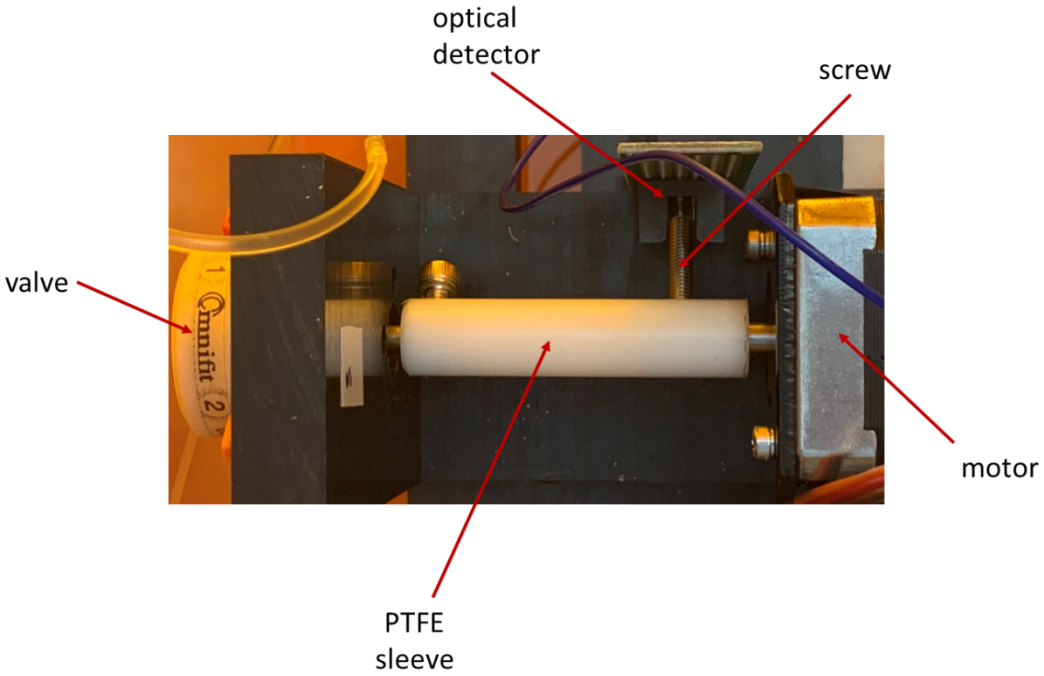


Figure 8-15: Optical detector used to position the valves presenting most important components.

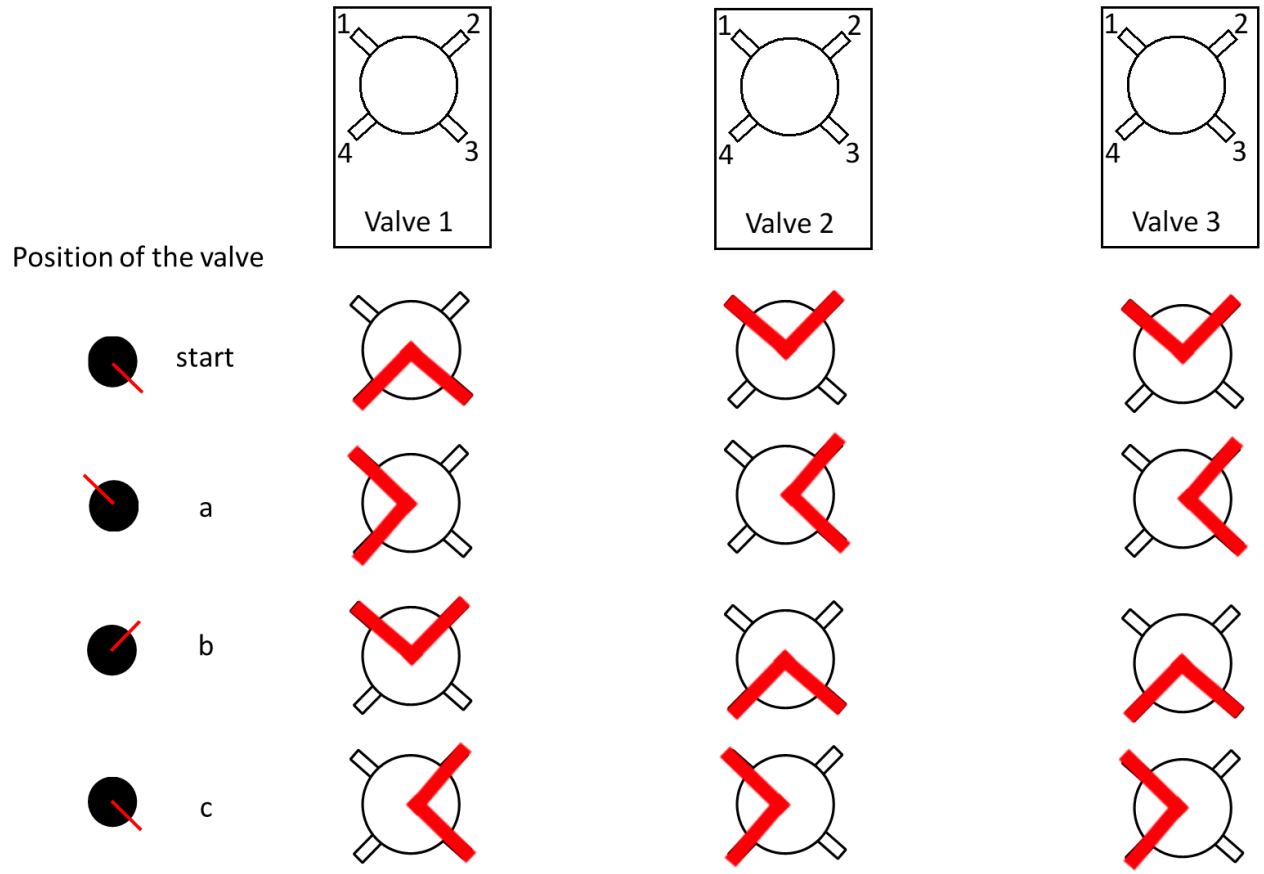


Figure 8-16: Positions of the valves in respect to the optical detector.

There are two ways to control the position of the valves. The first is using the and a program panel to move the valve to the wanted position (Figure 8-17). The second is to control the process by the Arduino microcontroller. The program has been written by Professor Fielden and used in the experiments (Chapter 11 and Chapter 12).

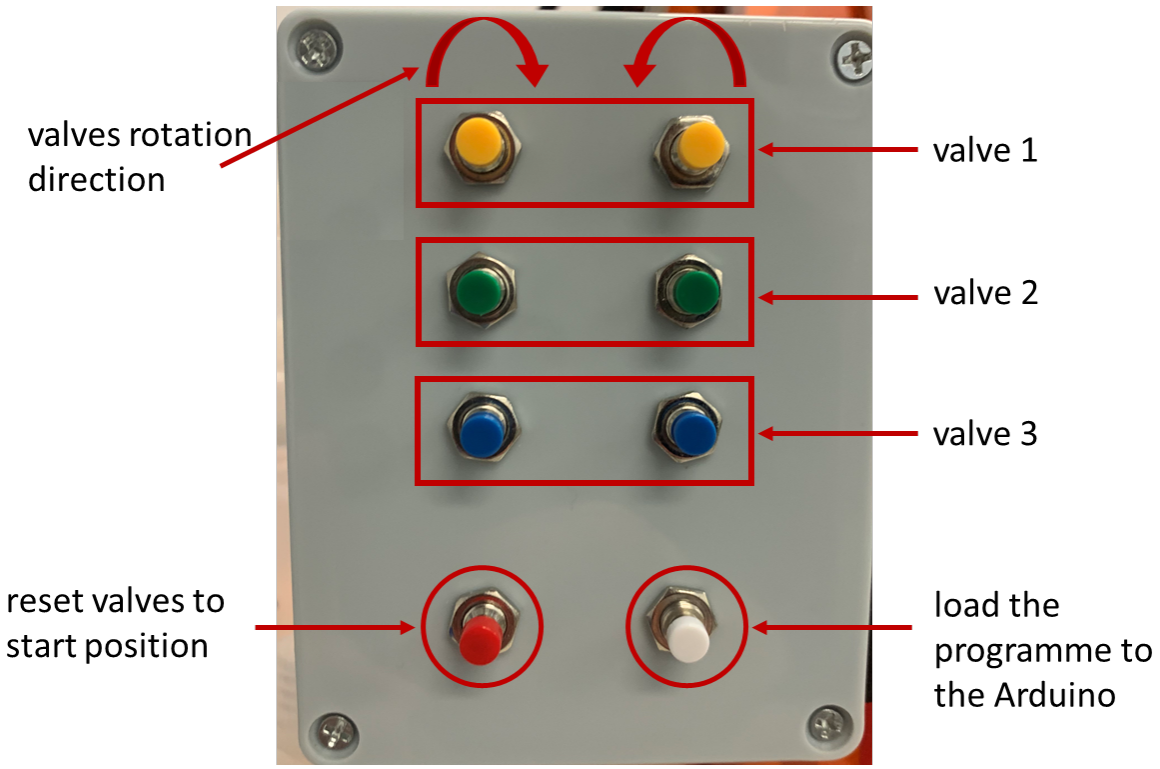


Figure 8-17: The panel used to control the valves.

Figure 8-18 presents a schematic of the valve's connections in the prototype. Length of tubing *a* and *b* is 10cm each with ID of 1mm. The length of sample loop is 5cm with ID of 1.5mm. All tubing was made from PTFE.

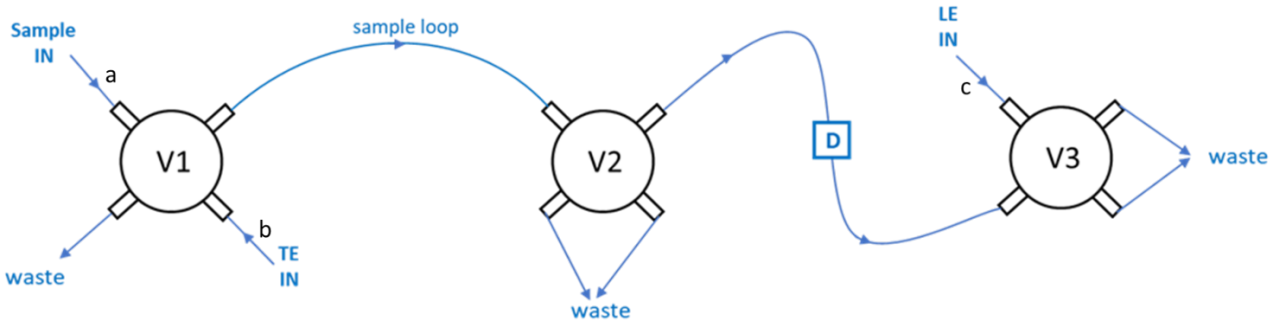


Figure 8-18: Schematic of connections between the valves.

Table 8-3: Position of the valves for all steps of preparation for the separation.

	V1	V2	V3
Sample load	b	c	—
LE load	—	a	c
TE load	c	c	—
RUN	c	start	c

8.6.1 Programming of the Arduino Uno/Arduino Nano

The Arduino microcontroller is widely used among students and researches as it is cheap and easy to use. It does not require knowledge of complicated programming languages, it uses simplified 'C-type language'. There are many examples of program codes available so all one needs to do is to modify it to fit the needs.

Usage of the microcontroller has many advantages, the most important is that it eliminates human error, provides constant conditions of the experiments and allows remote operation.

In this PhD project two types of Arduino were used, Arduino Uno and Nano (Figure 8-19).

Arduino Uno was used to control the positions of the valves, while the Arduino Nano was responsible for the recognition of the initial position of the valve using the optical detector. The codes are available in Chapter 11 and Chapter 12.

Each valve was controlled independently through an autonomous Arduino Nano. The function of Arduino Nano microcontroller was to drive a stepper-motor into one the four possible valve positions. The stepper motor was configured so that a full 360° rotation required an input of 800 driver steps. Therefore, a quarter turn was achieved by sending 200 steps (i.e. 90°) to the stepper motor. When the prototype was powered up, the Arduino Nano was programmed to reset the valve by locating the optical switch "closed" position (which was positioned half-way between an active valve position). Once the switch position had been located, 100 steps (i.e. 45°) were sent to the stepper motor to turn the valve to its first position. The program would wait for instructions to assume one of the four valve switch positions and also the direction from which that valve position was accessed (i.e. clockwise or anticlockwise). A "complete" signal was sent from Arduino Nano to the master Arduino, to indicate when the selected valve position had been reached.

Each valve was isolated for high voltage safety by using a polypropylene drive shaft of 5cm length. Each valve unit was mounted on a nylon carriage that fitted onto a nylon “rail” system such that the three valves (and the detector) could be positioned on the rail to configure the prototype separation system.

The Arduino Uno was programmed to introduce the timing of the separation process, including loading of the electrolytes, loading of the sample, and subsequent flushing between analyses. The times and valve positions were programmed using a data array, where each valve position was chosen during a series of timed periods. This data array was devised by the operator but had to be programmed into Arduino Uno using the C-language to populate the internal data array accordingly. The same program could be repeated by a push-button selection or reset to “abort” a separation “mid-flight”.

a) b)

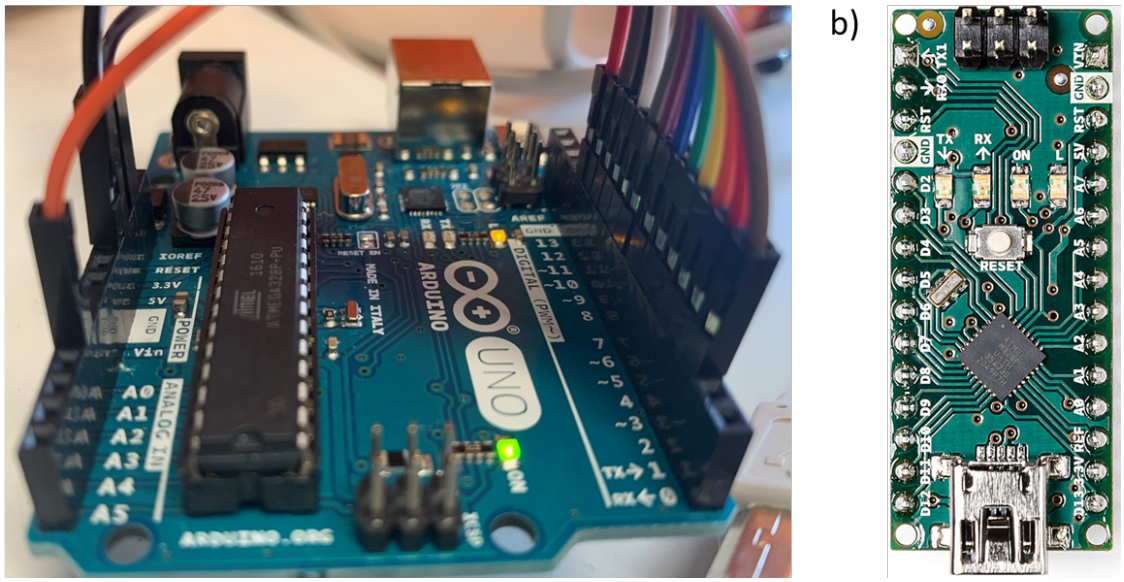


Figure 8-19: a) Arduino Uno used as a control unit for the prototype separation instrument, b) Arduino Nano used to control the optical detector.

Chapter 9 Evaluation of prototype separations

All samples investigated in the project are colourless thus it is impossible to see if the separation is taking place until sample reaches the detector. In some cases, the separation was stopped due to the time it took (sometimes it was several hours).

To evaluate if the prototype is working correctly, estimate separation time and being able to prove that the system works additional experiments were conducted using anionic dyes.

Preliminary experiments included visual confirmation of separations of anionic dyes using a method from the literature. Table 9-1 presents the electrolyte system used in the dye separations. The voltage applied was set to 3500V, with the separation operating in a constant voltage mode. The sample was 1:1 mixture of 5mM of amaranth and bromophenol blue.

Table 9-1: Electrolyte system used in anionic dye separation.

Electrolyte system	Anionic dyes
LE	10mM HCl
Complexing agent	0.05% Mowiol
pH buffer	Histidine
pH	6.0
TE	10mM MES
TE pH buffer	Histidine
TE pH	6.0

9.1 Dyes used in the project

Figure 9-1: Solutions of amaranth (on the right) and bromophenol blue (on the left).

Amaranth is an anionic dye mainly used in the food, clothing and cosmetics industry. In chemistry it is used as a dye for microscopic stain.

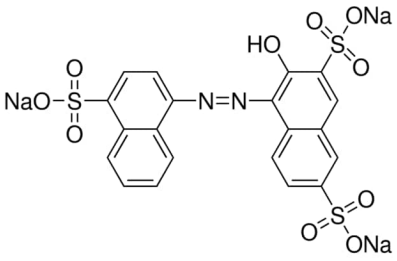


Figure 9-2: Molecular structure of amaranth dye.

Bromophenol blue is used a pH indicator and is used a dye in the electroporation of nucleic acids.

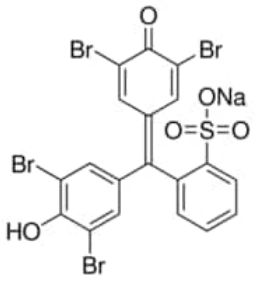


Figure 9-3: Bromophenol blue dye used in the separation of dyes.

9.2 **Separation of anionic dyes**

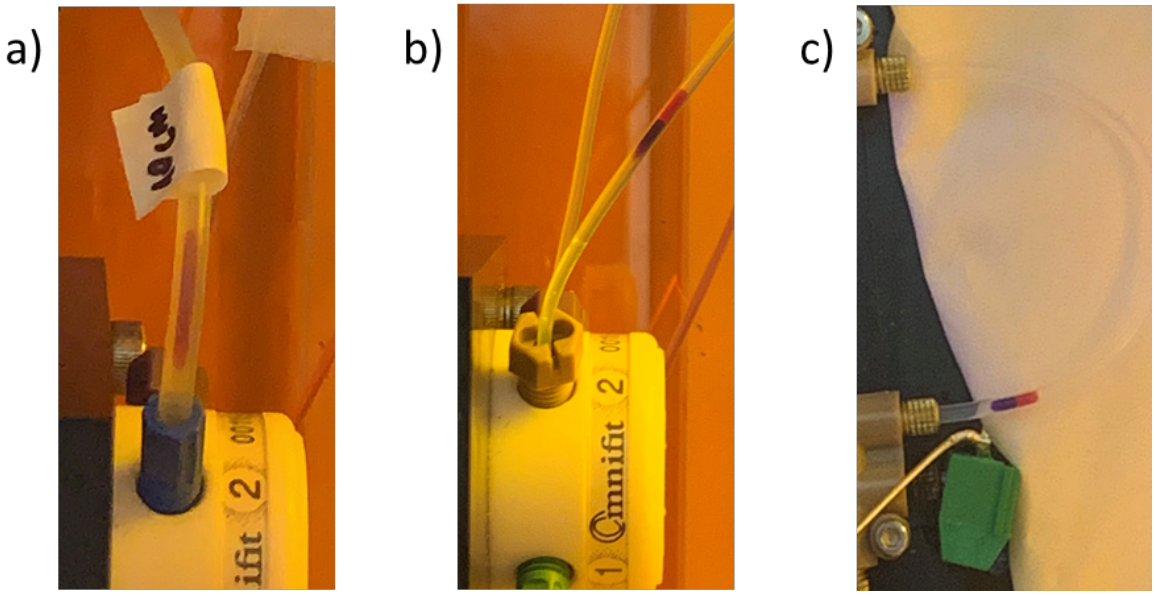


Figure 9-4: Separation of dyes. a) mixture of dyes after injection, b) partial separation with visible tailing of the dye, c) separated dyes in the loop after the detector.

A mixture of dyes was injected into the system as seen is Figure 9-4a, the mixture appears pink in colour. After applying voltage into the system separation begins and it is possible to observe two zones (Figure 9-4b), bromophenol blue shows some tailing and the zone is not fully formed yet. Figure 9-4c shows what seems to be a visually complete separation.

All pictures were taken from outside the safety box using an iPhone camera.

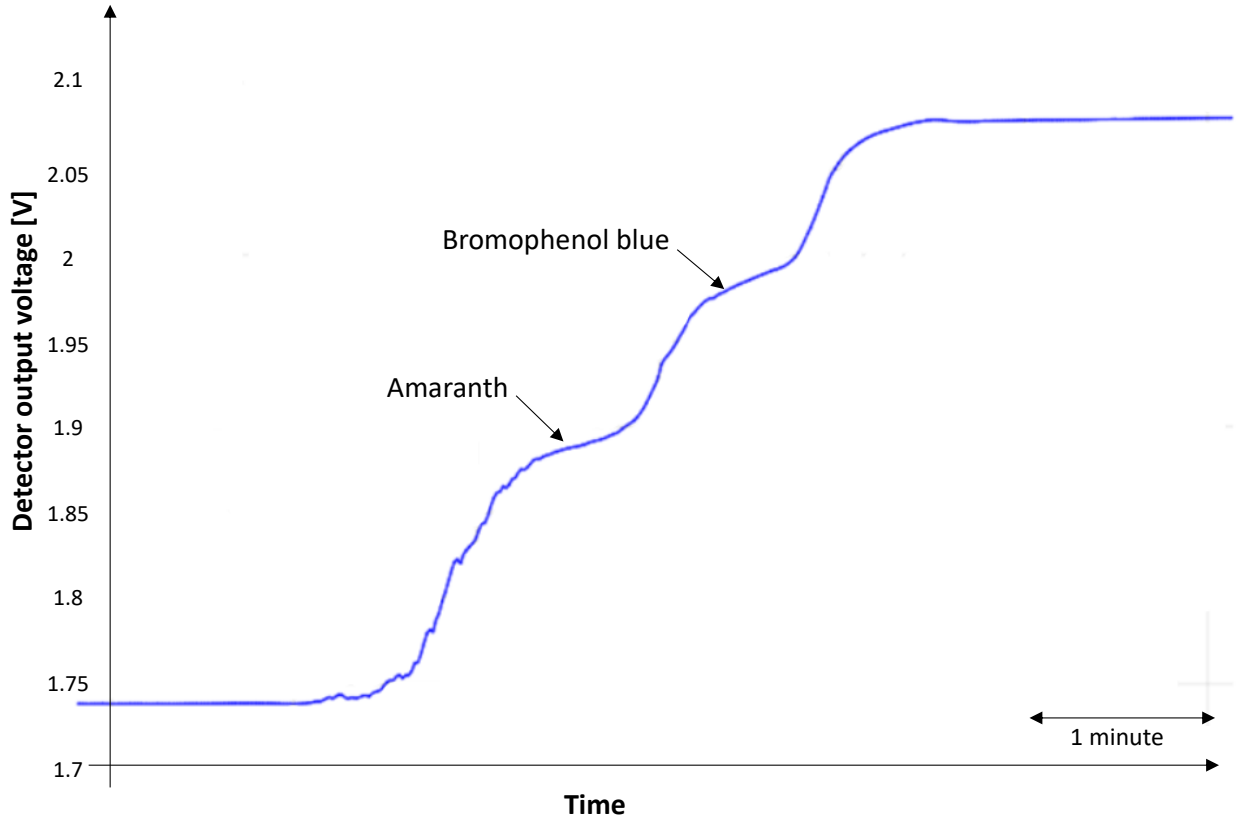


Figure 9-5: Isotachopherogram of the separation of the dyes.

Chapter 10 Summary

Throughout this study many experiments were conducted on several samples using various electrolytes systems. Majority of the methods from the articles have been proven to work. All worked on the industrial Itachrom ITP separation unit.

Successful separations of the ions were obtained using all techniques used in the project – ITP, IC and ICP-OES. The prototype was proven to be working however the limited time prevent detailed validation of the instrument. Successful separation of ionic dyes mixture allows the conclusion that it would work for other ionic species.

Ion chromatography was used to analyse magnesium, calcium and ammonium ions due to the column available at the university.

The prototype instrument was constructed using widely available materials.

10.1 **Future work**

In the course of this study most of the aims were successfully achieved. However, the project time scale, particularly with the Covid restrictions concerning both university laboratory access, and especially the furloughing of the development staff at the sponsoring company (Process Instruments Ltd) did not allow either the intended development and construction or the full exploration of the potential of the prototype instrument. The initial separations are promising but more work needs to be done to further evaluate the limit of detection, minimal volume of the sample and the inclusion of a pre-concentration technique. Preconcentration may be achieved through the inclusion of a large volume sample loop, followed by the equivalent of taking a “heart cut” (as may be used as a pre-separation step in chromatography) into a second analytical ITP column. This would require an additional valve, which could have been mounted on the prototype alignment rail (as currently used to support the three valves and detector modules).

Experiments optimising the various electrolytes and their concentrations should be conducted to find the optimum values. That may allow use of the shorter separation column thus shorter separation time.

The prototype is rather big so many improvements would need to be done to make it smaller and more portable. That would need input from the sponsor company regarding the construction of a bespoke high-voltage safety box. The development of the programmable high-voltage power supply (i.e. a reliable and working version of the prototype power supply built by the company for this programme) will be essential to ensure full safety in the application of high voltages, and the provision of the fully programmed constant current feature to reduce the separation times.

Whilst it has been possible to demonstrate that the automated sample introduction design within the prototype works, and as intended, as evidenced through the separation of the dye test sample. Indeed, the separation could be followed visually, as well as through the detector (also demonstrating that the high-voltage isolated conductivity detector also works), it is clear that the separation time is too long to be a practical proposition for the intended commercial instrument. The separation capillaries are of similar (or even slightly longer) length than those used on the laboratory ITP separation instrument (ItaChrom II EA 202M). However, the prototype was designed to restrict the applied voltage to no more than 3.5kV (the optical isolators in the detector circuit are rated at 4kV) which is far short from 15kV power supply capability in the laboratory instrument. Since the separation time is proportional to the applied potential (voltage applied per unit length) the only other option available would be to significantly reduce the overall length of the separation capillaries and especially the length of the feed tubes between the electrolyte reservoirs and the separation capillary, as defined by the connections into and out of the rotary valves. Clearly, a significant development input could be applied and the length through which the electric separation field is delivered is the key to the future development of the prototype into a commercially viable at-line measurement instrument. Analysis times of “one-per-hour” may well be sufficient for a water hardness application, but the ability to significantly reduce the separation and overall analysis time to a few minutes would be transformational.

The development of the prototype may well benefit from the production of a separation “cartridge”, whereby the separation capillary, electrolyte reservoirs and associated high voltage drive electrodes are fully integrated with miniaturised switching valves to reduce the overall high voltage pathlength considerably. The electrodes would also need a feed-in approach, such that larger volumes of electrolytes and wash solutions may be stored at longer distance from the separation “cartridge”. Such developments are beyond the remit of the university partner.

Nevertheless, even this fairly rudimentary protype has at least demonstrated the potential to employ ITP as s novel commercial measurement instrument. Process Instruments have identified the exciting prospect of being able to measure water hardness by a “gold standard” approach of quantifying the separate contributions of simultaneous magnesium and calcium concentration measurement.

Currently there is no instrument that can achieve this within the water industries and so represents a commercial opportunity. In the longer term, there are other key measurements of heavy metals and aluminium, that are yet to be achieved as a commercial at-line monitor. This could be a further opportunity for the sponsor company, through the exploitation of a fully-automated ITP-based measurement instrument. The attraction with ITP is that it does not need to use separation columns with finite life-times, nor particle-filler columns that may be prone to fouling and unwanted biofilm generation. ITP in its simplicity of using a generic separation “tube” is most affective in this respect.

So, is there a future for ITP as an industrial at-line monitor? This thesis has set about to show the potential, and has achieved this aim for the company, although with preliminary results, rather than a fuller-programme of measurement trials, as was intended had it been feasible to have further developed the prototype within projects’ timeframe.

Taking a broader viewpoint, just maybe, the outcome of this thesis could herald the renaissance of ITP as a “go to” fully automated measurement instrument of choice? The sponsor company would need to review the market of commercial instruments’ competitors.

Chapter 11 Appendix I

Arduino Uno programme used to control the valves in the prototype experiments.

```
int off=0;
int on=1;

int predelay=5;

int n=4;
int time[]={5,10,15,10};

byte v1a[]={0,1,0,1};
byte v1d[]={1,1,0,0};
byte v1rlsb[]={0,0,1,1};
byte v1rmsb[]={1,1,1,1};

byte v2a[]={0,0,1,1};
byte v2d[]={0,1,0,0};
byte v2rlsb[]={1,1,0,0};
byte v2rmsb[]={1,1,0,0};

byte v3a[]={1,0,0,0};
byte v3d[]={0,1,0,1};
byte v3rlsb[]={0,1,0,1};
byte v3rmsb[]={0,1,1,0};

void setup()
{
  // put your setup code here, to run once:
```

```
pinMode(2,OUTPUT);
pinMode(3,OUTPUT);
pinMode(4,OUTPUT);
pinMode(5,OUTPUT);
pinMode(6,OUTPUT);
pinMode(7,OUTPUT);
pinMode(8,OUTPUT);
pinMode(9,OUTPUT);
pinMode(10,OUTPUT);
pinMode(11,OUTPUT);
pinMode(12,OUTPUT);
pinMode(13,OUTPUT);

}
void loop()
  // put your main code here, to run repeatedly:
{

   digitalWrite(2,off);
   digitalWrite(3,off);
   digitalWrite(4,off);
   digitalWrite(5,on);
   digitalWrite(6,off);
   digitalWrite(7,off);
   digitalWrite(8,off);
   digitalWrite(9,on);
   digitalWrite(10,off);
   digitalWrite(11,off);
   digitalWrite(12,off);
   digitalWrite(13,on);

   if (analogRead(1) < 100)
```

```
  {
  predelay=predelay*1000;
  delay(predelay);

long del=0;
int count=0;
int temp=0;

for(int i=0;i<n;i++)
    {
      del=time[count];
      del=del*1000;
      del=del-500;

      //**********

      temp=v1d[count];
      digitalWrite(4,temp);

      temp=v2d[count];
      digitalWrite(8,temp);

      temp=v3d[count];
      digitalWrite(12,temp);

      //**********

      temp=v1rlsb[count];
      digitalWrite(2,temp);
      temp=v1rmsb[count];
      digitalWrite(3,temp);
```

```
temp=v2rlsb[count];
digitalWrite(6,temp);
temp=v2rmsb[count];
digitalWrite(7,temp);

temp=v3rlsb[count];
digitalWrite(10,temp);
temp=v3rmsb[count];
digitalWrite(11,temp);

 //**********

delay(250);

temp=v1a[count];
digitalWrite(5,temp);

temp=v2a[count];
digitalWrite(9,temp);

temp=v3a[count];
digitalWrite(13,temp);

delay(250);

digitalWrite(5,on);
digitalWrite(9,on);
digitalWrite(13,on);

//**********

delay(del);
```

```
      count=count+1;

    }

}

}
```

Chapter 12 Appendix II

Arduino Nano programme used to control optical detector in the prototype experiments.

```
int off=0;
int on=1;
long steps=0;
int dir=0;
int d4=0;
int d5=0;

void setup() {
  // put your setup code here, to run once:
pinMode(4,INPUT);
pinMode(5,INPUT);
pinMode(6,INPUT);
pinMode(7,INPUT);
pinMode(8,OUTPUT);
pinMode(9,OUTPUT);
pinMode(10,INPUT);
pinMode(11,INPUT);
pinMode(12,INPUT);

digitalWrite(9,off);
for (long i=0; i<12800; i++)
{
  if (digitalRead(12) == on)
{
  digitalWrite(9,on);

 for (long j=0; j<400; j++)
              {
                digitalWrite(8,on);
```

```
                delay(1);
                digitalWrite(8,off);
                delay(1);

              i=12800;
              }
}
else
           {
              digitalWrite(8,on);
              delay(1);
              digitalWrite(8,off);
              delay(1);
           }
}

 for (long m=0; m<864000; m++)
  {
   if(digitalRead(10)==LOW)
  {
    digitalWrite(9,on);
   for(long n=0; n<800; n++)
      {
      digitalWrite(8,on);
      delay(1);
      digitalWrite(8,off);
      delay(1);
      }

  }

 if(digitalRead(11)==LOW)
```

```
{
  digitalWrite(9,off);
 for(long p=0; p<800; p++)
    {
    digitalWrite(8,on);
    delay(1);
    digitalWrite(8,off);
    delay(1);
    }

}

if(digitalRead(7)==LOW)
{
  if(digitalRead(6)==LOW)
   {
     digitalWrite(9,off);
   }
   else
   {
     digitalWrite(9,on);
   }
    if(digitalRead(4)==LOW)
   {
     d4=0;
   }
   else
   {
     d4=1;
   }

    if(digitalRead(5)==LOW)
```

```
    {
      d5=0;
    }
    else
    {
      d5=1;
    }

            steps=0;
            steps=steps+d4;
            steps=steps+d5;
            steps=steps+d5;
            steps=steps*800;

   for (long p=0;p<steps;p++)
     {
     digitalWrite(8,on);
     delayMicroseconds(300);
     digitalWrite(8,off);
     delayMicroseconds(300);
   }
  }

  delay(100);
   }
}

void loop() {
  // put your main code here, to run repeatedly:

}
```

Chapter 13 Appendix III

Cations

13.1 Group I ions

Ions analysed	Other ions detected	Interfering ions	LE	pH	TE	Detector	Concentration range	Time of analysis	Sample preparation	Ref
Li	La,Ce,Gd,Pb, Cd,Zn,Mg, Cu,Ni,Cr(III), Co,Mn,Y		20mM NaOH, 10-15mM HIBA, 0.5% HEC	4.8 (HAc)	10mM Car Hydro	CON CON, UV	5-15ppm	750-3200s		[67]
Na	Mg,Ca,Ba,Cu, Mn,Ni,Co,Pb, Al,Cd		20mM KOH or NaOH	HIBA to pH 5.0, HAc to pH 4.1	5mM HAc or HCl	CON	0.5-4nM	600s		[68–72]
Na	Ca,Mg,NH_4^+		10mM KOH, 0.2% HEC	8.35 (BICINE)	5mM Tris (pH 4.9 by HAc)	CON	Less than 0.5mM	4h		[71,73]
Na	Ca,Mg,Mn,NH_4^+		10mM KOH, 1mM ADA, 0.2% HEC	4.4-5.1 (HAc)	5mM Tris (pH 4.6 by HAc)	CON	0.1-10mM	90s??		[71,74]
Na	Ca,Mg,Mn,NH_4^+		10mM KOH, 0.2% HEC	8.3 (BICINE)	5mM Tris (pH 7.9 by HCl)	CON	0.1-10mM	90s??		[71,74]
Na,Li,K,Rb	Mg,NH_4^+		10mM CsOH, 0.75mM cryptand 222, 0.1% HEC	9.4 (glycylglycine)	10mM TBA	NON CON, UV	Less than 40ppm	400s		[75]
Na,K	Sr,Ba,NH_4^+		10mM CsOH, 4.5mM 18-c-6-e, 0.1% HEC	5.0 (pivalic acid)	10mM Tris	CON	K 12µg/l	450s		[76]
Na,K	NH_4^+		7.5mM H_2SO_4, 7mM 18-c-6-e, 0.1% HEC		10mM BTP	NON CON	K 0.01-0.5mM	300s		[77]
Na,K	NH_4^+		10mM RbOH, 0.1% HEC	9.0 (His)	10mM lithium citrate	NON CON	K 0.01-0.5mM	300s		[77]
Na,K	NH_4^+		10mM CsOH, 0.1% HEC	9.0 (His)	10mM lithium citrate	NON CON	K 0.01-0.5mM	300s		[77]

Na,K	Ca,Mg,Ba,Al		25mM CsOH, 0-30mM 18-c-6-e, 20% HAc, 22.5mM HIBA	4.4-4.5	5mM HAc	CON	Na 15-30mM, K 5-15mM	750s	Standards dissolved in 1M nitric acid, then dried, dried samples dissolved in 5mM HAc	[37,71]
Na	Ca,Ba,Ni,Cd,Pb		10mM CH_3COOK, 0.05% Mowiol	5.4 (HAc)	10mM Tris	THE		??		[12,71]
Na	Ba,Ca,Ni,Mn,Cu		10mM KOH, 0.05% Mowiol	6.4 (cacodylic acid)	10mM Tris	THE		??		[12,71]
Na,Li	Ba,Sr,Ca,Mg,Mn, Fe(II),Co,Ni,Zn,La, Ce,Cd,Y,Lu,Gd,Pb, Cu,Fe(III),Zr	(Sr,Ca); (Mn,Fe(II),Co,Ni,Zn,La); (Ce,Gd,Y); (Cu,Pb); (Fe(III),Zr)	20mM NH_4OH, 0.2% HPC	4.8 (HAc)	10mM Car Hydro	POT	0.3-0.5mM	300s??		[71,72,78]
Na,Li	Ba,Sr,Ca,Mg,Mn, Fe,Cd,Co,Ni,Zn,La, Pb,Ce,Gd,Cu,Y,Zr,Lu	(Ca,Na); (Fe,Cd); (La,Pb); (Zr,Lu)	20mM NH_4OH, 10mM HIBA, 0.2% HPC	4.8 (HAc)	10mM Car Hydro	POT	0.3-0.5mM	300s		[72,78]
Na,Li	Ba,Sr,Mg,Ca,Mn,Cd, Co,Ni,Zn,Ce,Y,Lu,Gd, Pb,Cu	For 0mM tartaric acid (Mn,Co,Ni, Zn,La); (Ce,Cd,Y); (Li,Lu); (Cu,Pb)	20mM NH_4OH, 0-5mM tartaric acid, 0.05% HPC	4.8 (HAc)	20mM Car Hydro	NON CON	0.5mM	350s		[71,79,80]
Na	Mg,Mn,Co,Ni,Cu, Cr(III),Pb		20mM NH_4OH, 10mM HIBA, 0.5% HEC	4.8 (HAc)	10mM Car Hydro	CON CON, UV		800s		[67]

Na	Ni,Cu,Zn,Cr(III),Pb		20mM NH_4OH, 0.5% HEC	4.8 (HAc)	10mM Car Hydro	CON CON, UV		450s		[67]
Na,K	Ca,Mg,NH_4^+		7.5mM H_2SO_4, 1-9mM 18-c-6-e, 0.1% HPC		10mM BTP	NON CON	0-0.3mM	1000s		[70,81]
K	NH_4^+,Pb,Ag,Tl		5mM HCl, 0.01% Triton X-100, 5-20mM 18-c-6-e or 15-c-5-e		10mM His (pH 4.0 by 0.5mM HCl or $HClO_4$)	POT	0.01-3mM	720-1000s		[40]
Na	Pb,Cd,NH_4^+		10mM HCl, 0.2% HEC		10mM Car Hydro	CON	Over 2-4ppm	250s		[82]
Li,Na	NH_4^+		12.5mM Cs_2CO_3, 7.5mM 18-c-6-e, 4mM ADA, 1mg/ml HEC	4.7 (HAc)	TE=LE	CON	10mM	1000s		[68,83]
Na,Li,K,Rb, Cs	NH_4^+		10mM HCl, 0-50mM 18-c-6-e		10mM Tris	CON	??	??		[71,84]
Na,K	Ca,Mg,NH_4^+		7.5mM H_2SO_4,7mM 18-c-6-e		5mM BTP, 10mM caproic acid	CON	2.5-14ppm	1200s		[84]
Na,K	Mg,Ca,NH_4^+		1.25mM EDA^{2+}, 3.75mM HAc, 50mM 18-c-6-e, 0.1% HEC	5.0	3mM HAc	CON	2-40μM	100s		[85]
Na	Ca,Mg,NH_4^+		10mM KOH, 50mM H_3BO_3	8.3	10mM lithium citrate	CON	??	??		[70]
Na,Li,Cs,Rb	Ca,Mg,Sr,NH_4^+		5mM p-toluensulfonic acid, 0.01% Triton X-100, 20-50mM 18-c-6-e		5mM TBA-Br	POT	1mM	??		[71,72,86]
Na,K,Cs	Ca,Mg,NH_4^+		10mM TMOH, 0.12g/l HPMC, 12ml/l HAc, 8ml/l Triton X-100 (sol: 98% CH_3OH)	5.6	30mM $Cd(NO_3)_2$	POT, UV (254nm)	1-100mM	1560s		[71,87]

Na,K,Cs	Ca,Mg,NH_4^+		10mM TMOH, 0.12g/l HPMC, 12ml/l HAc, (sol: 98% CH_3OH)	5.6	30mM $Cd(NO_3)_2$	POT, UV (254nm)	1-100mM	1560s		[71,87]
Li	Tl,Cd,La,Ca,Fe(II)		10mM HCl, 0.05% Mowiol	2.0	10mM Tris	THE	??	1200s		[12,71]
Na,K	Ca,NH_4^+		5mM HCl, 0-5mM 18-c-6-e (30% glycerol)		10mM lithium citrate	POT	0.1-2.0ppm	1100s		[72,88]
Na,K	Ca,NH_4^+		5mM HCl, 2mM 18-c-6-e, 0.01% Triton X-100		10mM LiCl, 0.01% Triton X-100	POT	25-300µg/l	1500s		[72,88]
Na,Li	Ca,Mg,Ba,Sr, Fe(II),Cu,Mn,Co,Y, Ni,La,Gd,Lu,Pb,Zn, Cd		20mM NH_4OH, 0.1% HPC	4.8 (HAc)	10mM Car Hydro	PIXE	0.3-0.5mM	550s		[89]
Na,Li	Ca,Mg,Ba,Sr,Cd, Pb,Zn,La,Lu,Cu,Zr, Fe(II),Mn,Co,Ni		10mM HCl, 10mM HIBA, 0.1% HPC	4.8 (HAc)	10mM Car Hydro	PIXE	0.3-0.5mM	400s		[89]
Na,Li,K,Rb, Cs	Ca,Mg,Ba,Fe(II),Cr, Cu,Ni,Co,Mn,Pb,Al, Zn,Cd,Tl,La,Ce	(Tl,Rb,Cs,K); (BA,Pb); (Ce,La); (Co,Cu,Ni, Zn,Mg,Mn, Fe(II)); (Cd,Cr)	10mM HCl	2.0	10mM Tris	THE	??	??		[90]
Na,Li	Ca,Mg,Cu,Cr,Fe(II), Mn,Ni,Co,Zn,Cd, Pb,La,Ce,	(Mg,Fe(II));(Ni,Mn,Ce,Co ,La,Zn); (Li,Cu,Cr,Pb)	10mM KAc	5.4 (HAc)	10mM Tris	THE	??	??		[90]
Na,Li	Ca,Mg,Ba,Fe,Cu, Ag,Co,Ni,Mn,Pb, Cd,Zn,La,Ce	(Co,Ni,La); (Ba,Ag);	10mM KOH	6.4 (cacodylic acid)	10mM Tris	THE	??	??		[90]

		(Zn,Ce,Mn); (Cd,Fe,Li,Pb)								
Na,K,Li,Rb, Cs	Ca,Mg,Ba,Fe,Cu, Mn,Co,Ni		10mM HCl (sol:CH_3OH)		10mM $CdCl_2$ (sol:CH_3OH)	THE	??	??		[90]
Na,Li	Ca,Mg,Ba,Co,Ni, Mn,Pb,Zn,Tl	(Co,Mn,Ni); (Pb,Zn)	10mM KAc (sol:CH_3OH)	6.4 (HAc)	10mM $CdCl_2$ (sol:CH_3OH)	THE	??	??		[90]
Na	Ba,Sr,Ni,Y,La,Ce, Pr,Nd,Sm,		20mM NH_3, 10mM HIBA, 0.1% HPC	4.8 (HAc)	10mM Car Hydro	High-purity Ge detector, PIXE/POT	Up to 50nM	500s		[80,91,92]
Na,K	Ca,Mg,Ba,NH_4^+		7mM H_2SO_4, 7.5mM 18-c-6-e, 0.2% MHEC	2.3	10mM Tris, 10-17.5mM HAc	CON CON	0.1-30ppm	360s		[93,94]
Na,K	Ca,Mg,Ba,NH_4^+		7mM H_2SO_4, 7.5mM 18-c-6-e, 2mM HIBA	2.0	10mM Tris, 10-17.5mM HAc	CON CON	0.1-30ppm	360s		[93,94]
Na,K	Ca,Mg,Ba,NH_4^+		7mM H_2SO_4, 7.5mM 18-c-6-e, 2mM oxalic acid	1.9	10mM Tris, 10-17.5mM HAc	CON CON	0.1-30ppm	360s		[93,94]
Na,K	Ca,Mg,Ba,NH_4^+		7mM H_2SO_4, 7.5mM 18-c-6-e, 2mM tartaric acid	1.9	10mM Tris, 10-17.5mM HAc	CON CON	0.1-30ppm	360s		[93,94]
Na,K	Ca,Mg,Ba,NH_4^+		7mM H_2SO_4, 7.5mM 18-c-6-e, 0.2% MHEC	2.3	10mM creatinine, 5mM HCl	CON CON	0.1-30ppm	360s		[93,94]
Na,K	Ca,Mg,Ba,NH_4^+		7mM H_2SO_4, 7.5mM 18-c-6-e, 2mM HIBA	2.0	10mM creatinine, 5mM HCl	CON CON	0.1-30ppm	360s		[93,94]
Na,K	Ca,Mg,Ba,NH_4^+		7mM H_2SO_4, 7.5mM 18-c-6-e, 2mM oxalic acid	1.9	10mM creatinine, 5mM HCl	CON CON	0.1-30ppm	360s		[93,94]
Na,K	Ca,Mg,Ba,NH_4^+		7mM H_2SO_4, 7.5mM 18-c-6-e, 2mM tartaric acid	1.9	10mM creatinine, 5mM HCl	CON CON	0.1-30ppm	360s		[93,94]

Na	Ca,Mg,NH_4^+		7.5mM H_2SO_4	2.1	10mM BTP	CON CON	0-0.5mM	780s		[95]
Li	La,Dy,Yb		30mM NaOH, 15mM HIBA, 1mg/ml HEC	4.9 (propionic acid)	10mM Car Hydro	CON	2.5-10mM	600-1400s		[68,96]
Na	Ca,Mg,Sr,Ba, Co,Cd		5.675 or 18.92mM KOH	5.1 (tartaric acid)	5mM EACA (pH 4.5 by tartaric acid)	POT	5-20mM	??		[71,97]
Na	Ca,Mg,Ba,Sr		10mM CsOH, 2mM ADA, 1mg/ml HEC	5.1 (pivalic acid)	10mM Tris	CON	10-30ppm	400-500s		[98]
Na	Ca,Mg,Ba,Sr		10mM CsOH, 1mM oxalic acid, 1mg/ml HEC	5.1 (pivalic acid)	10mM Tris	CON	10-30ppm	400-500s		[98]
Na	Ca,Mg,Ba,Sr		10mM CsOH, 2mM succinic acid, 1mg/ml HEC	5.1 (pivalic acid)	10mM Tris	CON	10-30ppm	400-500s		[98]
Na	Ca,Mg,Ba,Sr		10mM CsOH, 2mM HIDA, 1mg/ml HEC	5.1 (pivalic acid)	10mM Tris	CON	10-30ppm	400-500s		[98]
Na	Ca,Mg,Ba,Sr	(Ca,Na)	10mM HEC, 2mM malic acid, 1mg/ml HEC	5.1 (pivalic acid)	10mM Tris	CON	10-30ppm	400-500s		[98]
Na	Ca,Mg,Ba,Sr		10mM CsOH, 1mg/ml HEC	5.1 (pivalic acid)	10mM Tris	CON	10-30ppm	400-500s		[98]
Li,Na,K			10mM CsOH, 5mM 18-c-6-e, 0.1% HEC	9.4 (glycylgycine)	10mM TBA	NON CON, UV	10-100ppm	Up to 400s		[99]
Li,Na,K,Rb			10mM CsOH, 0.5-3.5mM cryptand 222, 0.1% HEC	9.4 (glycylgycine)	10mM TBA	NON CON, UV	10-100ppm	Up to 400s		[99]
Li,Na			10mM CsOH, 0.1% HEC	9.4 (glycylgycine)	10mM TBA	NON CON, UV	10-100ppm	Up to 400s		[99]
Na,K			10mM HCl, 0.1% HEC		10mM Car Hydro	CON	2mM	250s		[68,100]

Na,K,Li	Ca,Mg		10mM NH_4OH, 0.1% HEC (sol: 30% polyethylene glycol)	5.4 (HAc)	5mM tetraethylammonium	CON	1.1mM	120s		[71,80,101]
Na,K	Ca,Mg		2mM H_6L	2.4	4mM creatinine	CON CON	0.1-3mM	1200s		[70,102]
Na	Ba,Mg,Sr, triethylamine		20mM KOH, 1mM CITR	5.0	10mM $MgCl_2$	CON	2.8mM	1200s		[71,103]
Na	La,Ce,Pr,Nd,Sm,Eu, Gd,Tb,Dy,Ho,Er, Tm,Yb,Lu		27mM KOH, 15mM HIBA, 0.0025% PVA	4.9 (CH_3COOH)	BALA (pH 4.0 by HAc)	POT	1mM	1200s		[71,72,104]
Na,K,Li,Rs,Cs	Ca,Mg,Ba,Sr		10mM NH_4OH, 0.2% HEC, (sol: 50% or 0% PEG)	5.0 (HAc)	3-5mM TBA	CON	10-140ppb	400s		[70,71,105]
Na,K,Li,Rs,Cs	Ca,Mg,Ba,Sr		10mM NH_4OH, 0.2% HEC, (sol: 45% PEG)	5.0 (HAc)	3-5mM TBA	CON	10-140ppb	400s		[70,71,105]
Na,K,Li,Rs,Cs	Ca,Mg,Ba,Sr		10mM NH_4OH, 3mM malic acid, 0.2% HEC, (sol: 40% PEG)	5.0 (HAc)	3-5mM TBA	CON	10-140ppb	400s		[70,71,105]
Na,K,Li,Rs,Cs	Ca,Mg,Ba,Sr		10mM NH_4OH, 0.2% HEC, (sol: 45% PEG)	5.0 (HAc)	3-5mM TBA	CON	10-140ppb	400s		[70,71,105]
Na,K,Li,Rs,Cs	Ca,Mg,Ba,Sr		5mM NH_4OH, 0.2% HEC, (sol: 45% PEG)	5.0 (HAc)	3-5mM TBA	CON	10-140ppb	400s		[70,71,105]
Na	Ca		10mM KOH, 25mM HAc	4.4	10mM BALA (pH 4.4 by HAc)	NON CON, UV (254nm)	??	1100s		[106]
Na,Li	Ca,Ba,Co,Zn		10mM KAc (sol: CH_3OH)		10mM CdAc (sol: CH_3OH)	POT, CON	0.01M	1800s		[107]
Na	n-butylamine		10mM KOH	5.5 (CITR)	10mM creatinine (pH 7.0 by HCl)	CON	130-150mM	??		[108]
Na,Rb	Ca,thiamine		10mM NH_4Pic, 30mM 18-c-6-e, 0.4% Triton X-100	5.4	5mM HAc	CON	0.02-0.12g/ml	400s		[71,109]

Na	Ca,Ba,Cd		10mM KAc	5.4 (HAc)	Tris	CON	??	??		[110]
Na	Ca, vitamin B_1, HFG		PRE-SEPARATION: 10mM KOH, 0.2% Triton X-100 ANALYTICAL: 5mM KOH	PS: 6.0 (MES) AN: 5.7 (MES)	10mM EACA	CON, UV (254nm)	2mM	1000s		[111]
Na,K	Ca, vitamin B_1		PRE-SEPARATION: 5mM KOH, 0.2% Triton X-100 ANALYTICAL: 25mM EACA, 0.2% Triton X-100	PS: 5.7 (MES) AN: 4.0 (HAc)	25mM EACA, 0.2% Triton X-100, (pH 4.0 by HAc)	CON, UV (254nm)	??	1300s		[111]
Na	Ca,Mg		10mM KOH, 0.2% MHEC	6.0 (CITR)	5mM Tris (pH 7.8 by CITR)	CON	10.6-80nM	360s	Pre-treatment for CZE	[112]
Na	Ca,Mg		10mM KOH, 0.2% MHEC	6.1 (MES)	5mM Tris (pH 7.8 by CITR)	CON	10.6-80nM	360s	Pre-treatment for CZE	[112]
Na,K	Ca,Mg		7.5mM H_2SO_4		10mM lithium citrate	CON	??	??		[70]
Na,Li	Ca,Mg,Sr,Ba		10mM NH_4OH, 3mM HIDA, 0.1% HEC	6.8 (ACES)	His		??	??		[70,72]
Na,K			5mM CsOH, 2mM 18-c-6-e, 0.01% HPMC, (sol: 70% CH_3OH)		5mM TBA-Br, 0.01% HPMC, (sol: 70% CH_3OH)	POT	10-60ppm	1200s		[72,113]
Na			10mM $KHCO_3$	5.0 (CITR)	5mM creatinine (pH 5.0 by CITR)	CON	2.5mM	??		[114]

13.2 **Group II ions**

Ions analysed	Other ions detected	Interfering ions	LE	pH	TE	Detector	Concentration range	Time of analysis	Sample preparation	Ref
Ca	Cr(III),Fe(II),Ni, Mn,Co,Pb,Zn,Cd		10mM NaOH, 2.5mM malic acid, 1mg/l HEC	4.9 (propionic acid)	10mM TBA	CON	1-50ppm	550s		[68,115,116]
Ca	Cu,Ni,Mn,Zn		20mM NaOH, 40mM glycine, 0.1% HEC	6.5 (propionic acid)	10mM Car Hydro	NON CON, UV	5-60ppm	500s		[117]
Mg	La,Ce,Gd,Pb, Cd,Zn,Li, Cu,Ni,Cr(III), Co,Mn,Y		20mM NaOH, 10-15mM HIBA, 0.5% HEC	4.8 (HAc)	10mM Car Hydro	CON CON, UV	5-15ppm	750-3200s		[67]
Ca,Mg	Mn,Co,Ni,Zn, La,Nd,Cd,Cu		20mM NaOH, 15mM HIBA, 0.05% HEC	4.9 (propionic acid)	10mM Car Hydro	CON	40-80mM (of metal)	400s		[68,118]
Ca	Mn,Ni,Cu,Zn		20mM NaOH, 10mM HIBA, 0.1% HEC	4.9 (propionic acid)	10mM Car Hydro	NON CON, UV	5-80ppm	??		[117]
Ca,Mg	Mn,Co,Ni,Cu,Fe(II) , Cd,Zn,Pb,Al		20mM NaOH, 20mM acetate, 15mM HIBA, 0.1% HEC (10% PEG)	4.8	10mM acetate	CON, PHO (405nm)	0.04-0.4mM (of metal)	240s		[119]
Ca,Mg	Zn,Mn,Co,Ni,Cu,Y, La,Er,Tm,Ce,Pr, Nd,Lu,Yb,Sm,Eu, Gd,Ho		30mM NaOH, 15mM HIBA, 0.1% HEC	4.9 (propionic acid)	10mM Car Hydro	CON	Ca 10-100ppm	600s		[117,120]
Mg,Ca,Ba	Na,Cu,Mn,Ni, Co,Pb, Al,Cd		20mM KOH or NaOH	HIBA to pH 5.0, HAc to pH 4.1	5mM HAc or HCl	CON	0.5-4nM; 25-100ppm (of metal)	600s		[68–72]
Ca,Mg	Na,NH_4^+		10mM KOH, 0.2% HEC	8.35 (BICINE)	5mM Tris (pH 4.9 by HAc)	CON	Less than 0.5mM	4h		[71,73]

Ca,Mg	Na,Mn,NH_4^+		10mM KOH, 1mM ADA, 0.2% HEC	4.4-5.1 (HAc)	5mM Tris (pH 4.6 by HAc)	CON	0.1-10mM	90s??		[71,74]
Ca,Mg	Na,Mn,NH_4^+		10mM KOH, 0.2% HEC	8.3 (BICINE)	5mM Tris (pH 7.9 by HCl)	CON	0.1-10mM	90s??		[71,74]
Mg	Na,Li,K,Rb ,NH_4^+		10mM CsOH, 0.75mM cryptand 222, 0.1% HEC	9.4 (glycylglycine)	10mM TBA	NON CON, UV	Less than 40ppm	400s		[75]
Sr,Ba	Na,K,NH_4^+		10mM CsOH, 4.5mM 18-c-6-e, 0.1% HEC	5.0 (pivalic acid)	10mM Tris	CON	Sr, Ba 20µg/l	450s		[76]
Ca,Mg,Ba	Na,K,Al		25mM CsOH, 0-30mM 18-c-6-e, 20% HAc, 22.5mM HIBA	4.4-4.5	5mM HAc	CON	Ca and Ba less than 10mM	750s	Standards dissolved in 1M nitric acid, then dried, dried samples dissolved in 5mM HAc	[37,71]
Ca,Ba	Na,Ni,Cd,Pb		10mM CH_3COOK, 0.05% Mowiol	5.4 (HAc)	10mM Tris	THE		??		[12,71]
Ba,Ca	Na,Ni,Mn,Cu		10mM KOH, 0.05% Mowiol	6.4 (cacodylic acid)	10mM Tris	THE		??		[12,71]
Ca,Mg,Ba,Sr	Na,Li,Mn,Fe(II), Co,Ni,Zn,La,Ce,Cd, Y,Lu,Gd,Pb,Cu, Fe(III),Zr	(Sr,Ca); (Mn,Fe(II),Co,Ni,Zn,La); (Ce,Gd,Y); (Cu,Pb); (Fe(III),Zr)	20mM NH_4OH, 0.2% HPC	4.8 (HAc)	10mM Car Hydro	POT	0.3-0.5mM	300s??		[71,72,78]
Ca,Mg,Ba,Sr	Mn,Fe,Cd,Co,Ni, Zn,La,Pb,Ce,Gd, Cu,Y,Zr,Lu, Na,Li	(Ca,Na); (Fe,Cd); (La,Pb); (Zr,Lu)	20mM NH_4OH, 10mM HIBA, 0.2% HPC	4.8 (HAc)	10mM Car Hydro	POT	0.3-0.5mM	300s		[72,78]
Ca,Mg,Ba,Sr	Mn,Cd,Co,Ni,Zn, Ce,Y,Lu,Gd,Pb,Cu, Na,Li	For 0mM tartaric acid (Mn,Co,Ni,Zn,La);	20mM NH_4OH, 0-5mM tartaric acid, 0.05% HPC	4.8 (HAc)	20mM Car Hydro	NON CON	0.5mM	350s		[71,79,80]

		(Ce,Cd,Y); (Li,Lu); (Cu,Pb)								
Mg	Na,Mn,Co,Ni,Cu, Cr(III),Pb		20mM NH_4OH, 10mM HIBA, 0.5% HEC	4.8 (HAc)	10mM Car Hydro	CON CON, UV	5ppm	800s		[67]
Ca,Mg	Na,K,NH_4^+		7.5mM H_2SO_4, 1-9mM 18-c-6-e, 0.1% HPC		10mM BTP	NON CON	0-0.3mM	1000s		[70,81]
Ca,Mg complexes with EDTA	Cu,Mn complexes with EDTA		10mM HCl, 0.5% methyl cellulose	8.5 (Tris)	10mM hexanoic acid	POT	0.5-7mM	1200s		[121]
Ca,Mg	Na,K,NH_4^+		7.5mM H_2SO_4,7mM 18-c-6-e		5mM BTP, 10mM caproic acid	CON	2.5-14ppm	1200s		[84]
Ca,Mg	Na,K,NH_4^+		1.25mM EDA^{2+}, 3.75mM HAc, 50mM 18-c-6-e, 0.1% HEC	5.0	3mM HAc	CON	2-40μM	100s		[85]
Ca,Mg	Na,NH_4^+		10mM KOH, 50mM H_3BO_3	8.3	10mM lithium citrate	CON	??	??		[70]
Ca,Mg,Sr	Na,Li,Cs,Rb,NH_4^+		5mM p-toluensulfonic acid, 0.01% Triton X-100, 20-50mM 18-c-6-e		5mM TBA-Br	POT	1mM	??		[71,72,86]
Ca,Mg	Na,K,Cs,NH_4^+		10mM TMOH, 0.12g/l HPMC, 12ml/l HAc, 8ml/l Triton X-100 (sol: 98% CH_3OH)	5.6	30mM $Cd(NO_3)_2$	POT, UV (254nm)	1-100mM	1560s		[71,87]
Ca,Mg	Na,K,Cs,NH_4^+		10mM TMOH, 0.12g/l HPMC, 12ml/l HAc, (sol: 98% CH_3OH)	5.6	30mM $Cd(NO_3)_2$	POT, UV (254nm)	1-100mM	1560s		[71,87]
Ca	Tl,Cd,La,Li,Fe(II)		10mM HCl, 0.05% Mowiol	2.0	10mM Tris	THE	??	1200s		[12,71]
Ca	Na,K,NH_4^+		5mM HCl, 0-5mM 18-c-6-e (30% glycerol)		10mM lithium citrate	POT	0.1-2.0ppm	1100s		[72,88]
Ca	Na,K,NH_4^+		5mM HCl, 2mM 18-c-6-e, 0.01% Triton X-100		10mM LiCl, 0.01% Triton X-100	POT	25-300μg/l	1500s		[72,88]
Ca,Mg,Ba,Sr	Na,Li,Fe(II),Cu, Mn,Co,Y,Ni,La,Gd, Lu, Pb,Zn, Cd		20mM NH_4OH, 0.1% HPC	4.8 (HAc)	10mM Car Hydro	PIXE	0.3-0.5mM	550s		[89]

Ca,Mg,Ba,Sr	Na,Li,Cd, Pb,Zn,La,Lu,Cu,Zr, Fe(II),Mn,Co,Ni		10mM HCl, 10mM HIBA, 0.1% HPC	4.8 (HAc)	10mM Car Hydro	PIXE	0.3-0.5mM	400s		[89]
Ca	Pb,Cd		10mM NH_4Ac, 10mM HAc, 2mM ammonium hydrogen citrate, 0.1% Triton X-100, 1% polyethylene glycol	5.0	10mM HAc	CON	1.8nM	2500s		[122]
Ca,Mg,Ba	Na,Li,K,Rb,Cs, Fe(II),Cr,Cu,Ni,Co, Mn,Pb,Al,Zn,Cd, Tl,La,Ce	(Tl,Rb,Cs,K); (BA,Pb); (Ce,La); (Co,Cu,Ni,Zn,Mg, Mn,Fe(II)); (Cd,Cr)	10mM HCl	2.0	10mM Tris	THE	??	??		[90]
Ca,Mg	Na,Li,Cu,Cr,Fe(II), Mn,Ni,Co,Zn,Cd, Pb,La,Ce,	(Mg,Fe(II));(Ni,Mn ,Ce,Co,La,Zn); (Li,Cu,Cr,Pb)	10mM KAc	5.4 (HAc)	10mM Tris	THE	??	??		[90]
Ca,Mg,Ba	Na,Li,Fe,Cu,Ag,Co, Ni,Mn,Pb,Cd,Zn, La,Ce	(Co,Ni,La); (Ba,Ag); (Zn,Ce,Mn); (Cd,Fe,Li,Pb)	10mM KOH	6.4 (cacodylic acid)	10mM Tris	THE	??	??		[90]
Ca,Mg,Ba	Na,K,Li,Rb,Cs,Fe, Cu, Mn,Co,Ni		10mM HCl (sol:CH_3OH)		10mM $CdCl_2$ (sol:CH_3OH)	THE	??	??		[90]
Ca,Mg,Ba	Na,Li,Co,Ni, Mn,Pb,Zn,Tl	(Co,Mn,Ni); (Pb,Zn)	10mM KAc (sol:CH_3OH)	6.4 (HAc)	10mM $CdCl_2$ (sol:CH_3OH)	THE	??	??		[90]
Ba,Sr	Ni,Y,La,Ce, Pr,Nd,Sm,Na		20mM NH_3, 10mM HIBA, 0.1% HPC	4.8 (HAc)	10mM Car Hydro	High-purity Ge detector, PIXE/POT	Up to 50nM	500s		[80,91,92]
Ca,Mg,Ba,	Na,K,NH_4^+		7mM H_2SO_4, 7.5mM 18-c-6-e, 0.2% MHEC	2.3	10mM Tris, 10-17.5mM HAc	CON CON	0.1-30ppm	360s		[93,94]
Ca,Mg,Ba,	Na,K,NH_4^+		7mM H_2SO_4, 7.5mM 18-c-6-e, 2mM HIBA	2.0	10mM Tris, 10-17.5mM HAc	CON CON	0.1-30ppm	360s		[93,94]
Ca,Mg,Ba,	Na,K,NH_4^+		7mM H_2SO_4, 7.5mM 18-c-6-e, 2mM oxalic acid	1.9	10mM Tris, 10-17.5mM HAc	CON CON	0.1-30ppm	360s		[93,94]

Ca,Mg,Ba,	Na,K,NH_4^+		7mM H_2SO_4, 7.5mM 18-c-6-e, 2mM tartaric acid	1.9	10mM Tris, 10-17.5mM HAc	CON CON	0.1-30ppm	360s		[93,94]
Ca,Mg,Ba,	Na,K,NH_4^+		7mM H_2SO_4, 7.5mM 18-c-6-e, 0.2% MHEC	2.3	10mM creatinine, 5mM HCl	CON CON	0.1-30ppm	360s		[93,94]
Ca,Mg,Ba,	Na,K,NH_4^+		7mM H_2SO_4, 7.5mM 18-c-6-e, 2mM HIBA	2.0	10mM creatinine, 5mM HCl	CON CON	0.1-30ppm	360s		[93,94]
Ca,Mg,Ba,	Na,K,NH_4^+		7mM H_2SO_4, 7.5mM 18-c-6-e, 2mM oxalic acid	1.9	10mM creatinine, 5mM HCl	CON CON	0.1-30ppm	360s		[93,94]
Ca,Mg,Ba,	Na,K,NH_4^+		7mM H_2SO_4, 7.5mM 18-c-6-e, 2mM tartaric acid	1.9	10mM creatinine, 5mM HCl	CON CON	0.1-30ppm	360s		[93,94]
Ca,Mg	Na,NH_4^+		7.5mM H_2SO_4	2.1	10mM BTP	CON CON	0-0.5mM	780s		[95]
Ca	Cu,Mn,Ni,Zn		30mM NaOH, 15mM HIBA, 0.1% HEC	4.9 (propionic acid)	10mM Car Hydro	NON CON, UV	10-100ppm	??		[117]
Ca,Mg	Mn,Ni,Zn,La,Nd, Gd		20mM NaOH, 15mM HBA, 0.05% HEC	4.95	10mM Car Hydro	CON	0.8-1mM	450s		[68,123]
Ca,Mg,Sr,Ba	Na,Co,Cd		5.675 or 18.92mM KOH	5.1 (tartaric acid)	5mM EACA (pH 4.5 by tartaric acid)	POT	5-20mM	??		[71,124]
Ca,Mg,Ba,Sr	Cd,Co,Ni,Zn		5.2-26mM KOH, 0.2% Triton X-100	4.4 (HIBA/glycolic/lactic)	5mM EACA	POT	5-30mM	450s		[71,125]
Ca,Mg,Ba,Sr	Na		10mM CsOH, 2mM ADA, 1mg/ml HEC	5.1 (pivalic acid)	10mM Tris	CON	10-30ppm	400-500s		[98]
Ca,Mg,Ba,Sr	Na		10mM CsOH, 1mM oxalic acid, 1mg/ml HEC	5.1 (pivalic acid)	10mM Tris	CON	10-30ppm	400-500s		[98]
Ca,Mg,Ba,Sr	Na		10mM CsOH, 2mM succinic acid, 1mg/ml HEC	5.1 (pivalic acid)	10mM Tris	CON	10-30ppm	400-500s		[98]
Ca,Mg,Ba,Sr	Na		10mM CsOH, 2mM HIDA, 1mg/ml HEC	5.1 (pivalic acid)	10mM Tris	CON	10-30ppm	400-500s		[98]

Ca,Mg,Ba,Sr	Na	(Ca,Na)	10mM HEC, 2mM malic acid, 1mg/ml HEC	5.1 (pivalic acid)	10mM Tris	CON	10-30ppm	400-500s		[98]
Ca,Mg,Ba,Sr	Na		10mM CsOH, 1mg/ml HEC	5.1 (pivalic acid)	10mM Tris	CON	10-30ppm	400-500s		[98]
Ca			10mM HCl		10mM Tris	POT	0-50nM	1200s		[126]
Ca			10mM CH_3COOK	5.4 (HAc)	10mM $CH_3(CH_2)_4COOH$	POT	0-50nM	1200s		[71,126]
Ca/Sr-complexes			10mM HCl, 0.1% HMPC	9.0 (Tris)	10mM sodium hexanoate	POT	2mM	1500s		[71,72,127]
Ca,Mg	Na,K,Li		10mM NH_4OH, 0.1% HEC (sol: 30% polyethylene glycol)	5.4 (HAc)	5mM tetraethylamMonium	CON	1.1mM	120s		[71,80,101]
Ca,Mg	Na,K		2mM H_6L	2.4	4mM creatinine	CON CON	0.1-3mM	1200s		[70,102]
Ba,Mg,Sr	Na,triethylamine		20mM KOH, 1mM CITR	5.0	10mM $MgCl_2$	CON	2.8mM	1200s		[71,103]
Ca,Mg,Sr,Ba - CyDTA complexes			10mM NH_4OH, 0-2nM CyDTA	4.3 (HAc)	10mM Tris (pH 4.4 by HAc)	POT	5-40nM	300s		[71,72,128]
Ca,Mg,Sr,Ba - CyDTA complexes			10mM NH_4OH, 0-2nM CyDTA	4-6 (HAc)	10mM Tris (pH 4.4 by HAc)	POT	5-40nM	300s		[71,72,128]
Ca,Mg,Sr,Ba - CyDTA complexes			10mM NH_4OH, 0-2nM CyDTA	4-6 (HAc)	10mM BALA (pH 4.4 by HAc)	POT	5-40nM	300s		[71,72,128]
Ca,Mg,Sr,Ba - CyDTA complexes			10mM NH_4OH, 1mM CyDTA	5.7 (succinic acid)	10mM BALA (pH 4.4 by HAc)	POT	5-40nM	300s		[71,72,128]
Ca,Mg,Ba,Sr	Na,K,Li,Rs,Cs		10mM NH_4OH, 0.2% HEC, (sol: 50% or 0% PEG)	5.0 (HAc)	3-5mM TBA	CON	10-140ppb	400s		[70,71,105]
Ca,Mg,Ba,Sr	Na,K,Li,Rs,Cs		10mM NH_4OH, 0.2% HEC, (sol: 45% PEG)	5.0 (HAc)	3-5mM TBA	CON	10-140ppb	400s		[70,71,105]

Ca,Mg,Ba,Sr	Na,K,Li,Rs,Cs		10mM NH_4OH, 0.2%, 3mM malic acid, HEC, (sol: 40% PEG)	5.0 (HAc)	3-5mM TBA	CON	10-140ppb	400s		[70,71,105]
Ca,Mg,Ba,Sr	Na,K,Li,Rs,Cs		10mM NH_4OH, 0.2% HEC, (sol: 45% PEG)	5.0 (HAc)	3-5mM TBA	CON	10-140ppb	400s		[70,71,105]
Ca,Mg,Ba,Sr	Na,K,Li,Rs,Cs		5mM NH_4OH, 0.2% HEC, (sol: 45% PEG)	5.0 (HAc)	3-5mM TBA	CON	10-140ppb	400s		[70,71,105]
Ca	Na		10mM KOH, 25mM HAc	4.4	10mM BALA (pH 4.4 by HAc)	NON CON, UV (254nm)	??	1100s		[106]
Ca,Ba	Na,Li,Co,Zn		10mM KAc (sol: CH_3OH)		10mM CdAc (sol: CH_3OH)	POT, CON	0.01M	1800s		[107]
Ca,Mg-EDTA complexes			10mM HCl, 0.5% 0.5% methyl cellulose	8.5 (Tris)	10mM hexanoic acid	POT	700-1500mg/l	1500s		[71,121,129]
Ca	Na,Rb,thiamine		10mM NH_4Pic, 30mM 18-c-6-e, 0.4% Triton X-100	5.4	5mM HAc	CON	0.02-0.12g/ml	400s		[71,109]
Ca,Ba	Na,Cd		10mM KAc	5.4 (HAc)	Tris	CON	??	??		[110]
Ca	Na, vitamin B_1, HFG		PRE-SEPARATION: 10mM KOH, 0.2% Triton X-100 ANALYTICAL: 5mM KOH	PS: 6.0 (MES) AN: 5.7 (MES)	10mM EACA	CON, UV (254nm)	2mM	1000s		[111]
Ca	Na,K, vitamin B_1		PRE-SEPARATION: 5mM KOH, 0.2% Triton X-100 ANALYTICAL: 25mM EACA, 0.2% Triton X-100	PS: 5.7 (MES) AN: 4.0 (HAc)	25mM EACA, 0.2% Triton X-100, (pH 4.0 by HAc)	CON, UV (254nm)	??	1300s		[111]
Ca,Mg	Na		10mM KOH, 0.2% MHEC	6.0 (CITR)	5mM Tris (pH 7.8 by CITR)	CON	10.6-80nM	360s	Pre-treatment for CZE	[112]
Ca,Mg	Na		10mM KOH, 0.2% MHEC	6.1 (MES)	5mM Tris (pH 7.8 by CITR)	CON	10.6-80nM	360s	Pre-treatment for CZE	[112]
Ca,Mg	Na,K		7.5mM H_2SO_4		10mM lithium citrate	CON	??	??		[70]

Ca,Mg,Sr,Ba	Na,Li		10mM NH_4OH, 3mM HIDA, 0.1% HEC	6.8 (ACES)	His		??	??		[70,72]

13.3 Transition metal ions

Ions analysed	Other ions detected	Interfering ions	LE	pH	TE	Detector	Concentration range	Time of analysis	Sample preparation	Ref
Cu,Zn			2.5mM NaOH, 1.25mM HIBA, 0.1% HEC	4.9 (propionic acid)	10mM Car Hydro	NON CON, UV	5-500ppm	400s	None	130
Cu,Zn			5mM NaOH, 2.5mM HIBA, 0.1% HEC	4.9 (propionic acid)	10mM Car Hydro	NON CON, UV	5-500ppm	400s	None	130
Cu,Zn			7.5mM NaOH, 3.75mM HIBA, 0.1% HEC	4.9 (propionic acid)	10mM Car Hydro	NON CON, UV	5-500ppm	400s	None	130
Cu,Zn			10mM NaOH, 5mM HIBA, 0.1% HEC	4.9 (propionic acid)	10mM Car Hydro	NON CON, UV	5-500ppm	400s	None	130
Cr(III),Fe(II),Ni, Co, Mn,Zn,Cd	Ca,Pb		10mM NaOH, 2.5mM malic acid, 1mg/l HEC	4.9 (propionic acid)	10mM TBA	CON	1-50ppm (Ni 5-50ppm)	550s		68,115,116
Cu,Ni,Mn,Zn	Ca		20mM NaOH, 40mM glycine, 0.1% HEC	6.5 (propionic acid)	10mM Car Hydro	NON CON, UV	10-60ppm (Ni 5-60ppm)	500s		117
Cu,Ni,Cr(III), Co,Mn,Y,Cd,Zn	La,Ce,Gd,Pb,Li,Mg		20mM NaOH, 10-15mM HIBA, 0.5% HEC	4.8 (HAc)	10mM Car Hydro	CON CON, UV	5-15ppm	750-3200s		67
Cu,Mn,Co,Ni,Cd, Zn	Ca,Mg,La,Nd		20mM NaOH, 15mM HIBA, 0.05% HEC	4.9 (propionic acid)	10mM Car Hydro	CON	40-80mM (of metal)	400s		68,118
Cu,Mn,Ni,Zn	Ca		20mM NaOH, 10mM HIBA, 0.1% HEC	4.9 (propionic acid)	10mM Car Hydro	NON CON, UV	5-50ppm (Cu 5-100ppm)	??		117
Mn,Co,Ni,Cu, Fe(II),Cd,Zn	Pb,Al,Ca,Mg		20mM NaOH, 20mM acetate, 15mM HIBA, 0.1% HEC, (10% PEG)	4.8	10mM acetate	CON, PHO (405nm)	0.04-0.4mM (of metal)	240s		119
Mn,Co,Ni,Cu,Y,Zn	Ca,Mg,La,Er, Tm,Ce,Pr,Nd, Lu,Yb,Sm,Eu, Gd,Ho		30mM NaOH, 15mM HIBA, 0.1% HEC	4.9 (propionic acid)	10mM Car Hydro	CON	Mn,Ni 10-50ppm; Cu 10-100ppm	600s		117,120

Cu,Mn,Ni,Co,Cd	Na,Mg,Ca,Ba,Pb, Al		20mM KOH or NaOH	HIBA to pH 5.0, HAc to pH 4.1	5mM HAc or HCl	CON	0.5-4nM; 25-100ppm (of metal)	600s		[68–72]
Mn	Na,Ca,Mg,NH_4^+		10mM KOH, 1mM ADA, 0.2% HEC	4.4-5.1 (HAc)	5mM Tris (pH 4.6 by HAc)	CON	0.1-10mM	90s??		[71,74]
Mn	Na,Ca,Mg,NH_4^+		10mM KOH 0.2% HEC	8.3 (BICINE)	5mM Tris (pH 7.9 by HCl)	CON	0.1-10mM	90s??		[71,74]
Ni,Cd	Na,Pb,Ca,Ba		10mM CH_3COOK, 0.05% Mowiol	5.4 (HAc)	10mM Tris	THE		??		[12,71]
Mn,Cu,Ni	Na,Ba,Ca		10mM KOH, 0.05% Mowiol	6.4 (cacodylic acid)	10mM Tris	THE		??		[12,71]
Cu,Fe(II),Fe(III), Co,Ni,Mn,Zn,Y,Z r,Cd	Na,Li,La,Ce,Lu,Gd, Pb,Ca,Mg,Ba,Sr	(Sr,Ca); (Mn,Fe(II),Co,Ni, Zn,La); (Ce,Gd,Y); (Cu,Pb); (Fe(III),Zr)	20mM NH_4OH, 0.2% HPC	4.8 (HAc)	10mM Car Hydro	POT	0.3-0.5mM	300s??		[71,72,79]
Mn,Fe,Co,Ni,Cu, Y, Zr,Cd,Zn	La,Pb,Ce,Gd,Lu, Na,Li,Ca,Mg,Ba,Sr	(Ca,Na); (Fe,Cd); (La,Pb); (Zr,Lu)	20mM NH_4OH, 10mM HIBA, 0.2% HPC	4.8 (HAc)	10mM Car Hydro	POT	0.3-0.5mM	300s		[72,78]
Cu,Mn,Co,Ni,Y,C d, Zn	Ce,Lu,Gd,Pb,Na, Li,Ca,Mg,Ba,Sr	For 0mM tartaric acid (Mn,Co,Ni,Zn,La); (Ce,Cd,Y); (Li,Lu); (Cu,Pb)	20mM NH_4OH, 0-5mM tartaric acid, 0.05% HPC	4.8 (HAc)	20mM Car Hydro	NON CON	0.5mM	350s		[71,79,80]
Cu,Cr(III),Mn,Co , Ni	Mg,Pb,Na		20mM NH_4OH, 10mM HIBA, 0.5% HEC	4.8 (HAc)	10mM Car Hydro	CON CON, UV	5ppm	800s		[67]
Cu,Cr(III),Ni,Zn	Pb,Na		20mM NH_4OH, 0.5% HEC	4.8 (HAc)	10mM Car Hydro	CON CON, UV	5ppm	450s		[67]
Mn,Zn,Cd	Pb		20mM NH_4OH, 0.4mM xylenol orange, 0.1% HEC	5.0 (HAc)	1mM HNO_3	PHO (580nm)	10mM	250s		[71,72,131]

Fe(II),Fe(III)			20mM NH_4OH, 0.1% HPC	4.8 (HAc/propionic/n-caproic/n-butyric/n-valeric acids)	20mM HCl, 0.1% HPC (pH 3.6 by BALA)	NON CON	0-40nM	900s		[71,80,132]
Ag	NH_4^+,Pb,K,Tl		5mM HCl, 0.01% Triton X-100, 5-20mM 18-c-6-e or 15-c-5-e		10mM His (pH 4.0 by 0.5mM HCl or $HClO_4$)	POT	0.01-3mM	720-1000s		[40]
Fe(II),Cu,Ni,Mn, Zn, Cd	Pb		5mM HCl, 3mM BALA (sol: 45% acetone:H_2O)		5mM Na_2EDTA or Na_2CyDTA	POT	0-4ppm	150s		[71,133]
Fe(III)-DCTA	Al-DCTA,SO_4^{2-}, F^-,Cl^-		10mM HCl, 0.1% HEC	5.7 (His)	MES	CON	0.3-0.5g/l	150s		[71,134]
Cu,Mn complexes with EDTA	Ca,Mg complexes with EDTA		10mM HCl, 0.5% methyl cellulose	8.5 (Tris)	10mM hexanoic acid	POT	0.5-7mM	1200s		[121]
Cu,Cd,Zn	Al,Pb		30mM NH_4Ac, 10mM glycolic acid		5mM HAc	CON	0.5mM	1560s		[135]
Cu,Fe(II),Cr(III)	Pb,Al,NH_4^+		10mM KOH, 0.05% Mowiol	7.4 (diiodo-L-tyrosine)	10mM Tris	THE	??	??		[12,71]
Cr(III)	Pb,Ce,La		10mM HIO_3, 0.05% Mowiol	1.5	10mM Tris	THE	??	??		[12,71]
Fe(II),Cd	Tl,La,Li,Ca		10mM HCl, 0.05% Mowiol	2.0	10mM Tris	THE	??	1200s		[12,71]
Cu,Fe(II),Cr(III), Ni,Co,Cd,Zn	Pb,Al		5mM HCl, 2mM BALA, (sol:45% acetone)		5mM Na_2EDTA or Na_2PDTA or Na_2DCTA	POT	1mM	1440s		[72,136]
Fe(II),Cu,Mn, Co,Y,Ni	Na,Li,Ca,Mg,Ba, Sr,La,Gd,Lu		20mM NH_4OH, 0.1% HPC	4.8 (HAc)	10mM Car Hydro	PIXE	0.3-0.5mM	550s		[89]
Cu,Zr,Fe(II),Mn, Co,Ni,Zn,Cd	Na,Li,Pb,La,Lu, Ca,Mg,Ba,Sr		10mM HCl, 10mM HIBA, 0.1% HPC	4.8 (HAc)	10mM Car Hydro	PIXE	0.3-0.5mM	400s		[89]

Fe(II),Mn,Co,Cd, Zn,Hg	Pb		1-20mM $HClO_4$ (sol: DMF)		HCL (sol: DMF)	POT	0-20mM	1200s	Chlorides dissolved in DMF	[137]
Fe(II),Cr,Cu,Ni,Co,Mn,Zn,Cd	Ca,Mg,Ba,Na,Li,K, Rb,Cs,Pb,Al,Tl,La, Ce	(Tl,Rb,Cs,K); (BA,Pb); (Ce,La); (Co,Cu,Ni,Zn,Mg ,Mn,Fe(II)); (Cd,Cr)	10mM HCl	2.0	10mM Tris	THE	??	??		[90]
Cu,Cr,Fe(II), Mn,Ni,Co,Zn,Cd	Na,Li,Ca,Mg,Pb, La,Ce	(Mg,Fe(II));(Ni, Mn,Ce,Co,La,Zn) ; (Li,Cu,Cr,Pb)	10mM KAc	5.4 (HAc)	10mM Tris	THE	??	??		[90]
Fe,Cu,Ag,Co,Ni, Mn,Cd,Zn	Na,Li,Ca,Mg,Ba, Pb,La,Ce	(Co,Ni,La); (Ba,Ag); (Zn,Ce,Mn); (Cd,Fe,Li,Pb)	10mM KOH	6.4 (cacodylic acid)	10mM Tris	THE	??	??		[90]
Fe,Cu,Mn,Co,Ni	Na,K,Li,Rb,Cs, Ca,Mg,Ba		10mM HCl (sol:CH_3OH)		10mM $CdCl_2$ (sol:CH_3OH)	THE	??	??		[90]
Co,Ni,Mn,Zn	Na,Li,Ca,Mg,Ba, Pb,Tl	(Co,Mn,Ni); (Pb,Zn)	10mM KAc (sol:CH_3OH)	6.4 (HAc)	10mM $CdCl_2$ (sol:CH_3OH)	THE	??	??		[90]
Ni,Y	Ba,Sr,La,Ce, Pr,Nd,Sm,Na		20mM NH_3, 10mM HIBA, 0.1% HPC	4.8 (HAc)	10mM Car Hydro	High-purity Ge detector, PIXE/POT	Up to 50nM	500s		[80,91,92]
Fe(II),Cr(III),Zr, Mo, Ru	Te,Br		20mM NH_3, 1mM tartaric acid, 0.1% HPC	5.0 (HAc)	10mM Car Hydro	High-purity Ge detector, PIXE	Up to 50nM	500s		[91]
Cu,Fe(III),Y,Ni-EDTA complexes	Pb,La,Ce,Gd,Lu-EDTA complexes		20mM NH_3, 0.1% HPC, 0.1-1mM EDTA	4.8 (HAc)	TE=LE	NON CON	0.5mM	250s		[138]
Cu,Fe(III),Y,Ni-EDTA complexes	Pb,La,Ce,Gd,Lu-EDTA complexes		20mM NH_3, 0.1% HPC, 0.1-1mM EDTA	4.8 (caproic acid)	TE=LE	NON CON	0.5mM	250s		[138]
Cu,Fe(III),Y,Ni-EDTA complexes	Pb,La,Ce,Gd,Lu-EDTA complexes		20mM NH_3, 0.1% HPC, 0.1-1mM EDTA	6.0 (MOPS)	TE=LE	NON CON	0.5mM	250s		[138]

Fe(II),Mn,Zn,Cd, Hg	Pb,In,Ga		5mM $HClO_4$, (sol: dimethylformamide)		5mM HCl (sol: dimethylformamide)	POT	??	??		[72]
Fe(II),Cu,Ni,Mn, Co, Cd,Zn	Pb		20mM KOH or NaOH		5mM HAc	CON	??	??		[69,72]
Cu,Ag,Co,Zn,Hg, Cd			5-15mM HCl or HNO_3, 0.005% Mowiol	Tris	10mM KCN, 5mM $Ba(OH)_2$	POT	0.5mM	1500-1800s		[72,139]
Co,Ni,Zn			10mM NaOH, 7mM HIBA, 1mg/ml HEC	5.2 (propionic acid)	10mM TBA	CON	1-50ppm	500s		[115]
Cu,Mn,Ni,Zn	Ca		30mM NaOH, 15mM HIBA, 0.1% HEC	4.9 (propionic acid)	10mM Car Hydro	NON CON, UV	10-100ppm	??		[117]
Co,Ni,Zn			20mM NaOH,2.5mM glycine, 48.8mM HIBA, 0.1% HEC		10mM Car Hydro	NON CON, UV	??	500s		[117]
Co,Ni,Zn			20mM NaOH, 3mM glycine, 30mM HIBA, 0.1% HEC		10mM Car Hydro	NON CON, UV	??	500s		[117]
Ni,Zn			20mM NaOH, 40mM glycine, 0.1% HEC	6.5 (propionic acid)	10mM Car Hydro/HAc/ propionic acid	NON CON, UV	20-50ppm	600s		[117]
Mn,Ni,Zn	Ca,Mg,La,Nd,Gd		20mM NaOH, 15mM HIBA, 0.05% HEC	4.95	10mM Car Hydro	CON	0.8-1mM	450s		[68,123]
Co,Cd	Na,Ca,Mg,Sr,Ba		5.675 or 18.92mM KOH	5.1 (tartaric acid)	5mM EACA (pH 4.5 by tartaric acid)	POT	5-20mM	??		[71,124]
Co,Ni,Zn,Cd	Ca,Mg,Ba,Sr		5.2-26mM KOH, 0.2% Triton X-100	4.4 (HIBA/glycolic/lactic)	5mM EACA	POT	5-30mM	450s		[71,125]
Cr(VI)	Se(IV),Se(VI), F^-,NO_3^-,SO_4^{2-},SO_3^{2-}		5mM HCl, 1mg/ml HEC	4.1 (GABA)	10mM TBA	CON	0.25-25ppm	350s		[68,140]
Fe(III)-EDTA			10mM HCl, 20mM His, 0.1% HPMC	6.0	5mM MES	CON CON, UV (254nm)	0-500µg/l of Fe(III)	600s		[141]

Y	La,Ce,Pr,Nd,Sm, Eu,Gd,Tb,Dy,Ho, Er,Tm,Yb,Lu		20mM NH_4OH, HIBA	4.8 (2-ethyl-n-nbutyric acid)	Car Hydro	CON	0.33mM	1850s		[142]
Cr(VI)			10mM HCl, 0.1% HEC	3.5 (BALA)	HAc	PHO (254,405nm), CON	0.1mM	100s		[70,71,143]
Cr(VI)			10mM HCl, 0.1% HEC	6.9 (BTP)	CITR	PHO (254,405nm), CON	0.1mM	100s		[70,71,143]
Cr(VI)	Se(VI),Se(IV), As(V), SO_4^{2-}		20mM HNO_3, 0.5g/l Mowiol	5.5 (His)	20mM gallic acid		10-20ppm	650s		[144]
Y	La,Ce,Pr,Nd,Sm, Eu,Gd,Tb,Dy,Ho, Er,Yb,Lu		20mM NH_4OH, 7.5mM HIBA, 2mM malic acid, 0.1% HPC	4.8 (2-ethylbutyric acid)	20mM Car Hydro, 0.1% HPC	NON CON	0.33mM	350s		[71,145]
Co,Zn	Na,Li,Ca,Ba		10mM KAc (sol: CH_3OH)		10mM CdAc (sol: CH_3OH)	POT, CON	0.01M	1800s		[107]
Ag nanoparticles			PRE-SEPARATION: 10mM HNO_3 ANALYTICAL: 10mM HNO_3	PS: 7.1 (imidazole) AN: 4.5 (EACA)	PS: 10mM MES AN: 5mM caproic acid	CON CON, UV	5mM	??		[93,146]
Y	La,Ce,Pr,Nd,Sm, Eu,Gd,Tb,Dy,Ho, Er,Tm,Yb,Lu		PRE-SEPARATION: 20mM NH_3, 10mM HIBA, 1.75% HPC ANALYTICAL: 20mM NH_3, 10mM HIBA, 0.2% HPC	PS: 4.8 (HAc) AN: 4.8 (HAc)	PS: 10mM Car Hydro, 20% sucrose AN: 10mM Car Hydro, 0.2% HPC	POT	4.5mM	450s		[147]
Fe(III),Mn,Hg			PRE-SEPARATION: 8mM NaCl, 3mM BTP, 1.5mM BALA, 0.1% HEC ANALYTICAL: 1mM NaCl, 1.5mM BALA, 0.1% HEC		5mM CITR	CON	50-200μg/l	??		[93,148]

Y	La,Ce,Pr,Nd,Sm, Eu,Gd,Tb,Ho,Er, Tm,Yb,Lu		20mM NH_3, 5-10mM HIBA, 0.4-1.25mM tartaric acid, 0.1% HPC	4.8 (HAC)	10mM Car Hydro, 0.1% HPC	NON CON	0.33-1.6mM	500s		[80,149]
Fe(III)	Ga		5mM HCl, 3mM BALA, (sol: 45% acetone)		5mM EDTA	POT	??	??		[72]
Y	La,Ce,Pr,Nd,Sm, Eu,Gd,Tb,Dy,Ho, Er,Tm,Yb,Lu		20mM NH_4OH, 7.5mM HIBA, 10mM malic acid, 0.1% HPC	4.8 (2-ethylbutyric acid)	20mM Car Hydro, 0.1% HPC	NON CON	2.5-200ppm	750s		[72,150]
Ni,Pt,Ag,Au			6mM HCl, 0.01% PVA, (sol: H_2O:acetonitrile)	8.4 (Tris)	10mM KCN, 50mM $Ba(OH)_2$	POT	1-5nM	800s		[72,151]

13.4 **Other ions**

Ions analysed	Other ions detected	Interfering ions	LE	pH	TE	Detector	Concentration range	Time of analysis	Sample preparation	Ref
Pb	Ca,Cr(III),Fe(II), Ni, Co, Mn,Zn,Cd		10mM NaOH, 2.5mM malic acid, 1mg/l HEC	4.9 (propionic acid)	10mM TBA	CON	1-50ppm	550s		[68,115,116]
Pb	La,Ce,Gd,Li,Cd,Zn,Cu, Ni,Cr(III),Co,Mn,Y,Mg		20mM NaOH, 10-15mM HIBA, 0.5% HEC	4.8 (HAc)	10mM Car Hydro	CON CON, UV	5-15ppm	750-3200s		[67]
Pb,Al	Ca,Mg,Mn,Co, Ni,Cu,Fe(II),Cd,Zn		20mM NaOH, 20mM acetate, 15mM HIBA, 0.1% HEC, (10% PEG)	4.8	10mM acetate	CON, PHO (405nm)	0.04-0.4mM (of metal)	240s		[119]
Pb,Al	Na,Mg,Ca,Ba, Cd,Cu,Mn,Ni,Co		20mM KOH or NaOH	HIBA to pH 5.0, HAc to pH 4.1	5mM HAc or HCl	CON	0.5-4nM; 25-100ppm (of metal)	600s		[68–72]
Al	Na,K,Ca,Mg,Ba		25mM CsOH, 0-30mM 18-c-6-e, 20% HAc, 22.5mM HIBA	4.4-4.5	5mM HAc	CON	??	750s	Standards dissolved in 1M nitric acid, then dried, dried samples dissolved in 5mM HAc	[37,71]

Pb	Na,Ni,Ca,Ba,Cd		10mM CH_3COOK, 0.05% Mowiol	5.4 (HAc)	10mM Tris	THE		??		[12,71]
Pb	Na,Li,La,Ce,Cd,Lu,Gd, Ca,Mg,Ba,Sr, Cu,Fe(II), Fe(III),Co,Ni,Mn,Zn,Y, Zr,Cd	(Sr,Ca); (Mn,Fe(II),Co,Ni,Zn ,La); (Ce,Gd,Y); (Cu,Pb); (Fe(III),Zr)	20mM NH_4OH, 0.2% HPC	4.8 (HAc)	10mM Car Hydro	POT	0.3-0.5mM	300s??		[71,72,78]
Pb	La,Ce,Gd,Lu,Na,Li,Ca, Mg,Ba,Sr,Cd,Zn,Mn, Fe,Co,Ni,Cu,Y, Zr	(Ca,Na); (Fe,Cd); (La,Pb); (Zr,Lu)	20mM NH_4OH, 10mM HIBA, 0.2% HPC	4.8 (HAc)	10mM Car Hydro	POT	0.3-0.5mM	300s		[71,78]
Pb	Ce,Lu,Gd,Na,Li,Ca,Mg, Ba,Sr,Cu,Mn,Co,Ni,Y, Zn,Cd	For 0mM tartaric acid (Mn,Co,Ni,Zn,La); (Ce,Cd,Y); (Li,Lu); (Cu,Pb)	20mM NH_4OH, 0-5mM tartaric acid, 0.05% HPC	4.8 (HAc)	20mM Car Hydro	NON CON	0.5mM	350s		[71,79,80]
Pb	Mg,Na,Cu,Cr(III),Mn, Co,Ni		20mM NH_4OH, 10mM HIBA, 0.5% HEC	4.8 (HAc)	10mM Car Hydro	CON CON, UV	5ppm	800s		[67]
Pb	Zn,Cu,Cr(III),Ni,Na		20mM NH_4OH, 0.5% HEC	4.8 (HAc)	10mM Car Hydro	CON CON, UV	5ppm	450s		[67]
Pb	Mn,Zn,Cd		20mM NH_4OH, 0.4mM xylenol orange, 0.1% HEC	5.0 (HAc)	1mM HNO_3	PHO (580nm)	10mM	250s		[71,72,131]
Pb,Tl	NH_4^+,K,Ag		5mM HCl, 0.01% Triton X-100, 5-20mM 18-c-6-e or 15-c-5-e		10mM His (pH 4.0 by 0.5mM HCl or $HClO_4$)	POT	0.01-3mM	720-1000s		[40]
Pb	Fe(II),Cu,Ni,Mn,Zn,Cd		5mM HCl, 3mM BALA (sol: 45% acetone:H_2O)		5mM Na_2EDTA or Na_2CyDTA	POT	0-4ppm	150s		[71,133]
Al-DCTA	Fe(III)-DCTA,SO_4^{2-}, F^-,Cl^-		10mM HCl, 0.1% HEC	5.7 (His)	MES	CON	0.3-0.5g/l	150s		[71,134]
Pb	Cd,Na,NH_4^+		10mM HCl, 0.2% HEC		10mM Car Hydro	CON	Over 2-4ppm	250s		[82]
Al,Pb	Cu,Zn,Cd		30mM NH_4Ac, 10mM glycolic acid		5mM HAc	CON	0.5mM	1560s		[135]

Pb,Al	Cu,Fe(II),Cr(III), NH_4^+		10mM KOH, 0.05% Mowiol	7.4 (diiodo-L-tyrosine)	10mM Tris	THE	??	??		[12,71]
Pb	Ce,La,Cr(III)		10mM HIO_3, 0.05% Mowiol	1.5	10mM Tris	THE	??	??		[12,71]
Tl	La,Li,Ca,Fe(II),Cd		10mM HCl, 0.05% Mowiol	2.0	10mM Tris	THE	??	1200s		[12,71]
Pb,Al	Cu,Fe(II),Cr(III),Ni,Co, Zn,Cd		5mM HCl, 2mM BALA, (sol:45% acetone)		5mM Na_2EDTA or Na_2PDTA or Na_2DCTA	POT	1mM	1440s		[72,136]
Pb	Na,Li,Fe(II),Cu,Mn, Co,Y,Ni,La,Gd,Lu,Ca, Mg,Sr,Ba,Cd,Zn		20mM NH_4OH, 0.1% HPC	4.8 (HAc)	10mM Car Hydro	PIXE	0.3-0.5mM	550s		[89]
Pb	Na,Li,La,Lu,Ca,Mg, Ba,Sr,Cu,Zr,Cd,Zn, Fe(II),Mn,Co,Ni		10mM HCl, 10mM HIBA, 0.1% HPC	4.8 (HAc)	10mM Car Hydro	PIXE	0.3-0.5mM	400s		[89]
Pb	Fe(II),Mn,Co,Cd,Hg,Zn		1-20mM $HClO_4$ (sol: DMF)		HCL (sol: DMF)	POT	0-20mM	1200s	Chlorides dissolved in DMF	[137]
Pb	Ca,Cd		10mM NH_4Ac, 10mM HAc, 2mM ammonium hydrogen citrate, 0.1% Triton X-100, 1% polyethylene glycol	5.0	10mM HAc	CON	1.8nM	2500s		[122]
Al,Al satls			10mM NaAc, 1% HMPC	3.6	10mM Tris (pH 3.3 by HAc)	CON, UV	0-15ppm	9s??????		[152]
Pb,Al,Tl	Ca,Mg,Ba,Na,Li,K,Rb, Cs,La,Ce,Fe(II),Cr,Cu, Ni,Co,Mn,Zn,Cd	(Tl,Rb,Cs,K); (BA,Pb); (Ce,La); (Co,Cu,Ni,Zn,Mg, Mn,Fe(II)); (Cd,Cr)	10mM HCl	2.0	10mM Tris	THE	??	??		[90]

Pb,Zn,Cd	Na,Li,Ca,Mg,La,Ce, Cu,Cr,Fe(II),Mn,Ni,Co	(Mg,Fe(II));(Ni,Mn, Ce,Co,La,Zn); (Li,Cu,Cr,Pb)	10mM KAc	5.4 (HAc)	10mM Tris	THE	??	??		[90]
Pb	Na,Li,Ca,Mg,Ba,La,Ce, Fe,Cu,Ag,Co,Ni,Mn, Zn,Cd	(Co,Ni,La); (Ba,Ag); (Zn,Ce,Mn); (Cd,Fe,Li,Pb)	10mM KOH	6.4 (cacodylic acid)	10mM Tris	THE	??	??		[90]
Pb,Tl	Na,Li,Ca,Mg,Ba,Zn,Co, Ni,Mn	(Co,Mn,Ni); (Pb,Zn)	10mM KAc (sol:CH_3OH)	6.4 (HAc)	10mM $CdCl_2$ (sol:CH_3OH)	THE	??	??		[90]
Pb-EDTA complexes	Cu,Fe(III),Y,Ni,La,Ce, Gd,Lu-EDTAvcomplexes		20mM NH_3, 0.1% HPC, 0.1-1mM EDTA	4.8 (HAc)	TE=LE	NON CON	0.5mM	250s		[138]
Pb-EDTA complexes	Cu,Fe(III),Y,Ni,La,Ce, Gd,Lu-EDTA complexes		20mM NH_3, 0.1% HPC, 0.1-1mM EDTA	4.8 (caproic acid)	TE=LE	NON CON	0.5mM	250s		[138]
Pb-EDTA complexes	Cu,Fe(III),Y,Ni,La,Ce, Gd,Lu-EDTA complexes		20mM NH_3, 0.1% HPC, 0.1-1mM EDTA	6.0 (MOPS)	TE=LE	NON CON	0.5mM	250s		[138]
Pb,In,Ga	Fe(II),Mn,Hg,Zn,Cd		5mM $HClO_4$, (sol: dimethylformamide)		5mM HCl (sol: dimethylformamide)	POT	??	??		[72]
Pb,Cd,Zn	Fe(II),Cu,Ni,Mn,Co		20mM KOH or NaOH		5mM HAc	CON	??	??		[69,72]
Zn,Hg,Cd	Cu,Ag,Co		5-15mM HCl or HNO_3, 0.005% Mowiol	Tris	10mM KCN, 5mM $Ba(OH)_2$	POT	0.5mM	1500-1800s		[72,139]
Pb			10mM CsOH	4.7 (HAc)	10mM TBA	NON CON	10-100ppm	800s		Jeff??
Ga	Fe(III)		5mM HCl, 3mM BALA, (sol: 45% acetone)		5mM EDTA	POT	??	??		[72]
NH_4^+	Na,Ca,Mg		10mM KOH, 0.2% HEC	8.35 (BICINE)	5mM Tris (pH 4.9 by HAc)	CON	Less than 0.5mM	4h		[71,73]
NH_4^+	Na,Ca,Mg,Mn		10mM KOH, 1mM ADA, 0.2% HEC	4.4-5.1 (HAc)	5mM Tris (pH 4.6 by HAc)	CON	0.1-10mM	90s??		[71,74]
NH_4^+	Na,Ca,Mg,Mn		10mM KOH, 0.2% HEC	8.3 (BICINE)	5mM Tris (pH 7.9 by HCl)	CON	0.1-10mM	90s??		[71,74]
NH_4^+	Na,Li,K,Rb,Mg		10mM CsOH, 0.75mM cryptand 222, 0.1% HEC	9.4 (glycylglycine)	10mM TBA	NON CON, UV	Less than 40ppm	400s		[75]

NH_4^+	Na,K,Sr,Ba		10mM CsOH, 4.5mM 18-c-6-e, 0.1% HEC	5.0 (pivalic acid)	10mM Tris	CON	NH_4^+ 15μg/l	450s		[76]
NH_4^+	Na,K		7.5mM H_2SO_4, 7mM 18-c-6-e, 0.1% HEC		10mM BTP	NON CON	NH_4^+ 0.4mM	300s		[77]
NH_4^+	Na,K		10mM RbOH, 0.1% HEC	9.0 (His)	10mM lithium citrate	NON CON	NH_4^+ 0.4mM	300s		[77]
NH_4^+	Na,K		10mM CsOH, 0.1% HEC	9.0 (His)	10mM lithium citrate	NON CON	NH_4^+ 0.4mM	300s		[77]
NH_4^+	Na,K,Ca,Mg		7.5mM H_2SO_4, 1-9mM 18-c-6-e, 0.1% HPC		10mM BTP	NON CON	0-0.3mM	1000s		[70,81]
NH_4^+	K,Ag,Pb,Tl		5mM HCl, 0.01% Triton X-100, 5-20mM 18-c-6-e or 15-c-5-e		10mM His (pH 4.0 by 0.5mM HCl or $HClO_4$)	POT	0.01-3mM	720-1000s		[40]
NH_4^+	Pb,Cd,Na		10mM HCl, 0.2% HEC		10mM Car Hydro	CON	Over 2-4ppm	250s		[82]
NH_4^+	Li,Na		12.5mM Cs_2CO_3, 7.5mM 18-c-6-e, 4mM ADA, 1mg/ml HEC	4.7 (HAc)	TE=LE	CON	10mM	1000s		[68,83]
NH_4^+	Na,Li,K,Rb,Cs		10mM HCl, 0-50mM 18-c-6-e		10mM Tris	CON	??	??		[71,84]
NH_4^+	Na,K,Ca,Mg		7.5mM H_2SO_4,7mM 18-c-6-e		5mM BTP, 10mM caproic acid	CON	2.5-14ppm	1200s		[84]
NH_4^+	Na,K, Ca,Mg		1.25mM EDA^{2+}, 3.75mM HAc, 50mM 18-c-6-e, 0.1% HEC	5.0	3mM HAc	CON	2-40μM	100s		[85]
NH_4^+	Cu,Fe(II),Cr(III),Pb,Al		10mM KOH, 0.05% Mowiol	7.4 (diiodo-L-tyrosine)	10mM Tris	THE	??	??		[12,71]
NH_4^+	Na, Ca,Mg		10mM KOH, 50mM H_3BO_3	8.3	10mM lithium citrate	CON	??	??		[70]
NH_4^+	Na,Li,Cs,Rb, Ca,Mg,Sr		5mM p-toluensulfonic acid, 0.01% Triton X-100, 20-50mM 18-c-6-e		5mM TBA-Br	POT	1mM	??		[71,72,86]
NH_4^+	Na,K,Cs,Ca,Mg		10mM TMOH, 0.12g/l HPMC, 12ml/l HAc,	5.6	30mM $Cd(NO_3)_2$	POT, UV (254nm)	1-100mM	1560s		[71,87]

			8ml/l Triton X-100 (sol: 98% CH_3OH)							
NH_4^+	Na,K,Cs,Ca,Mg		10mM TMOH, 0.12g/l HPMC, 12ml/l HAc, (sol: 98% CH_3OH)	5.6	30mM $Cd(NO_3)_2$	POT, UV (254nm)	1-100mM	1560s		[71,87]
NH_4^+	Na,K,Ca,Mg,Ba		5mM HCl, 0-5mM 18-c-6-e (sol: 30% glycerol)		10mM lithium citrate	POT	0.1-2.0ppm	1100s		[72,88]
NH_4^+	Na,K,Ca,Mg,Ba		5mM HCl, 2mM 18-c-6-e, 0.01% Triton X-100		10mM LiCl, 0.01% Triton X-100	POT	25-300µg/l	1500s		[72,88]
NH_4^+	Na,K,Ca,Mg,Ba		7mM H_2SO_4, 7.5mM 18-c-6-e, 0.2% MHEC	2.3	10mM Tris, 10-17.5mM HAc	CON CON	0.1-30ppm	360s		[93,94]
NH_4^+	Na,K,Ca,Mg,Ba		7mM H_2SO_4, 7.5mM 18-c-6-e, 2mM HIBA	2.0	10mM Tris, 10-17.5mM HAc	CON CON	0.1-30ppm	360s		[93,94]
NH_4^+	Na,K,Ca,Mg,Ba		7mM H_2SO_4, 7.5mM 18-c-6-e, 2mM oxalic acid	1.9	10mM Tris, 10-17.5mM HAc	CON CON	0.1-30ppm	360s		[93,94]
NH_4^+	Na,K,Ca,Mg,Ba		7mM H_2SO_4, 7.5mM 18-c-6-e, 2mM tartaric acid	1.9	10mM Tris, 10-17.5mM HAc	CON CON	0.1-30ppm	360s		[93,94]
NH_4^+	Na,K,Ca,Mg,Ba		7mM H_2SO_4, 7.5mM 18-c-6-e, 0.2% MHEC	2.3	10mM creatinine, 5mM HCl	CON CON	0.1-30ppm	360s		[93,94]
NH_4^+	Na,K,Ca,Mg,Ba		7mM H_2SO_4, 7.5mM 18-c-6-e, 2mM HIBA	2.0	10mM creatinine, 5mM HCl	CON CON	0.1-30ppm	360s		[93,94]
NH_4^+	Na,K,Ca,Mg,Ba		7mM H_2SO_4, 7.5mM 18-c-6-e, 2mM oxalic acid	1.9	10mM creatinine, 5mM HCl	CON CON	0.1-30ppm	360s		[93,94]
NH_4^+	Na,K,Ca,Mg,Ba		7mM H_2SO_4, 7.5mM 18-c-6-e, 2mM tartaric acid	1.9	10mM creatinine, 5mM HCl	CON CON	0.1-30ppm	360s		[93,94]
NH_4^+	Na,Ca,Mg		7.5mM H_2SO_4	2.1	10mM BTP	CON CON	0-0.5mM	780s		[95]
Se(IV),Se(VI)	Cr(VI),F^-,NO_3^-, SO_4^{2-},SO_3^{2-}		5mM HCl, 1mg/ml HEC	4.1 (GABA)	10mM TBA	CON	0.25-25ppm	350s		[68,140]
Se(VI),Se(IV) ,As(V)	Cr(VI), SO_4^{2-}		20mM HNO_3, 0.5g/l Mowiol	5.5 (His)	20mM gallic acid		10-20ppm	650s		[144]

As(V),Te(IV), Te(VI)			5mM glycolic acid, 0.5g/l Mowiol	9.8 (N-methyl-D-glucamine)	20mM BALA (pH 10. By $Ba(OH)_2$)		10ppm	400s		[144]

13.5 **Lanthanide ions**

Ions analysed	Other ions detected	Interfering ions	LE	pH	TE	Detector	Concentration range	Time of analysis	Sample preparation	Ref
La,Ce,Gd	Pb,Cd,Zn,Li, Cu,Ni,Cr(III), Co,Mn,Y,Mg		20mM NaOH, 10-15mM HIBA, 0.5% HEC	4.8 (HAc)	10mM Car Hydro	CON CON, UV	5-15ppm	750-3200s		[67]
La,Nd	Ca,Mg,Zn,Cd, Cu,Mn,Co,Ni		20mM NaOH, 15mM HIBA, 0.05% HEC	4.9 (propionic acid)	10mM Car Hydro	CON	40-80mM (of metal)	400s		[68,118]
La,Ce,Cd,Lu,Gd	Na,Li,Ca,Mg,Ba,Sr, Cu,Fe(II),Pb,Cd, Fe(III),Co,Ni,Mn,Zn, Y,Zr	(Sr,Ca); (Mn,Fe(II),Co,Ni,Zn,La); (Ce,Gd,Y); (Cu,Pb); (Fe(III),Zr)	20mM NH_4OH, 0.2% HPC	4.8 (HAc)	10mM Car Hydro	POT	0.3-0.5mM	300s??		[71,72,78]
La,Ce,Gd,Lu	Na,Li,Ca,Mg,Ba,Sr, Mn,Fe,Co,Ni,Cu,Y, Zr,Pb,Zn,Cd	(Ca,Na); (Fe,Cd); (La,Pb); (Zr,Lu)	20mM NH_4OH, 10mM HIBA, 0.2% HPC	4.8 (HAc)	10mM Car Hydro	POT	0.3-0.5mM	300s		[72,78]
Lu,Gd,Ce	Pb,Zn,Cd,Na,Li, Ca,Mg,Ba,Sr, Cu,Mn,Co,Ni,Y	For 0mM tartaric acid (Mn,Co,Ni,Zn,La); (Ce,Cd,Y); (Li,Lu); (Cu,Pb)	20mM NH_4OH, 0-5mM tartaric acid, 0.05% HPC	4.8 (HAc)	20mM Car Hydro	NON CON	0.5mM	350s		[71,79,80]
Ce,La	Cr(III),Pb		10mM HIO_3, 0.05% Mowiol	1.5	10mM Tris	THE	??	??		[12,71]
La	Cd,Tl,Li,Ca,Fe(II)		10mM HCl, 0.05% Mowiol	2.0	10mM Tris	THE	??	1200s		[12,71]
La,Gd,Lu	Na,Li,Fe(II),Cu,Mn, Co,Y,Ni,Ca,Mg,Sr, Ba,Pb,Zn,Cd		20mM NH_4OH, 0.1% HPC	4.8 (HAc)	10mM Car Hydro	PIXE	0.3-0.5mM	550s		[89]
La,Lu	Na,Li,Ca,Mg,Cd,Pb, Zn,Ba,Sr,Cu,Zr, Fe(II),Mn,Co,Ni		10mM HCl, 10mM HIBA, 0.1% HPC	4.8 (HAc)	10mM Car Hydro	PIXE	0.3-0.5mM	400s		[89]

La,Ce	Ca,Mg,Ba,Na,Li,K, Rb,Cs,Fe(II),Cr,Cu, Ni,Co,Mn,Pb,Al,Zn, Cd,Tl	(Tl,Rb,Cs,K); (BA,Pb); (Ce,La); (Co,Cu,Ni,Zn,Mg,Mn,Fe(II)); (Cd,Cr)	10mM HCl	2.0	10mM Tris	THE	??	??		[90]
La,Ce	Na,Li,Ca,Mg,Pb,Zn, Cd,Cu,Cr,Fe(II),Mn, Ni,Co	(Mg,Fe(II));(Ni,Mn,Ce,C o,La,Zn); (Li,Cu,Cr,Pb)	10mM KAc	5.4 (HAc)	10mM Tris	THE	??	??		[90]
La,Ce	Na,Li,Ca,Mg,Ba,Pb, Cd,Zn,Fe,Cu,Ag,Co, Ni,Mn	(Co,Ni,La); (Ba,Ag); (Zn,Ce,Mn); (Cd,Fe,Li,Pb)	10mM KOH	6.4 (cacodylic acid)	10mM Tris	THE	??	??		[90]
La,Ce,Pr,Nd,Sm	Ba,Sr,Na,Ni,Y		20mM NH_3, 10mM HIBA, 0.1% HPC	4.8 (HAc)	10mM Car Hydro	High-purity Ge detector, PIXE/POT	Up to 50nM	500s		[80,91,92]
La,Ce,Gd, Lu - EDTA complexes	Cu,Fe(III),Y,Ni,Pb - EDTA complexes		20mM NH_3, 0.1% HPC, 0.1-1mM EDTA	4.8 (HAc)	TE=LE	NON CON	0.5mM	250s		[138]
La,Ce,Gd, Lu - EDTA complexes	Cu,Fe(III),Y,Ni,Pb - EDTA complexes		20mM NH_3, 0.1% HPC, 0.1-1mM EDTA	4.8 (caproic acid)	TE=LE	NON CON	0.5mM	250s		[138]
La,Ce,Gd, Lu - EDTA complexes	Cu,Fe(III),Y,Ni,Pb - EDTA complexes		20mM NH_3, 0.1% HPC, 0.1-1mM EDTA	6.0 (MOPS)	TE=LE	NON CON	0.5mM	250s		[138]
La,Nd,Gd	Ca,Mg,Mn,Ni,Zn		20mM NaOH, 15mM HBA, 0.05% HEC	4.95	10mM Car Hydro	CON	0.8-1mM	450s		[68,123]
La,Dy,Yb	Li		30mM NaOH, 15mM HIBA, 1mg/ml HEC	4.9 (propionic acid)	10mM Car Hydro	CON	2.5-10mM	600-1400s		[68,96]
La,Eu,Sm,Nd,Pr, Ce,La			9.85mM KOH, 1-4mM HIBA	4.8 (propionic acid)	EACA	POT	??	??		[71,153]

La,Ce,Pr,Nd,Sm, Eu, Gd,Tb,Dy,Ho,Er, Tm,Yb,Lu	Y		20mM NH_4OH, HIBA	4.8 (2-ethyl-n-nbutyric acid)	Car Hydro	CON	0.33mM	1850s		[142]
La,Ce,Pr,Nd,Sm, Eu, Gd,Tb,Dy,Ho,Er, Tm,Yb,Lu			20mM NH_4OH, 10mM HIBA, 0.2% HPC	4.8 (HAc)	10mM Car Hydro, 0.2% HPC	PIXE	5mM	250s		[154]
La,Ce,Pr,Nd,Sm, Eu, Gd,Tb,Dy,Ho,Er, Tm,Yb,Lu	Na		27mM KOH, 15mM HIBA, 0.0025% PVA	4.9 (CH_3COOH)	BALA (pH 4.0 by HAc)	POT	1mM	1200s		[71,72,104]
La,Ce,Pr,Nd,Sm, Eu, Gd,Tb,Dy,Ho,Er, Yb,Lu	Y		20mM NH_4OH, 7.5mM HIBA, 2mM malic acid, 0.1% HPC	4.8 (2-ethylbutyric acid)	20mM Car Hydro, 0.1% HPC	NON CON	0.33mM	350s		[71,145]
Ce,Sm,Dy,Tm,Lu			1mM KOH, 19mM NH_4OH, 10mM HIBA, 0.2% HPC	4.8 (HAc)	10mM Car Hydro	POT, PHO	25nM	??		[155]
La,Ce,Pr,Nd,Eu, Yb- DOTA, DTPA complexes			20mM HCl	3.1 (glycine)	20mM NH_3 (pH 4.8 by HAc)	CON	0-35nM	??		[156]
La,Ce,Pr,Nd,Sm, Eu,Gd,Tb,Dy,Ho, Er,Tm,Yb,Lu	Y		PRE-SEPARATION: 20mM NH_3, 10mM HIBA, 1.75% HPC ANALYTICAL: 20mM NH_3, 10mM HIBA, 0.2% HPC	PS: 4.8 (HAc) AN: 4.8 (HAc)	PS: 10mM Car Hydro, 20% sucrose AN: 10mM Car Hydro, 0.2% HPC	POT	4.5mM	450s		[147]
La,Dy	Amaranth dye		10mM HCl, 0.05% Mowiol	6.0 (His)	10mM MES (pH 6.0 by His)	CON	2.5mM, dye 10mM	400s		[157]
La,Ce,Pr,Nd,Sm, Eu,Gd,Tb,Ho,Er, Tm,Yb,Lu	Y		20mM NH_3, 5-10mM HIBA, 0.4-1.25mM tartaric acid, 0.1% HPC	4.8 (HAC)	10mM Car Hydro, 0.1% HPC	NON CON	0.33-1.6mM	500s		[80,149]

La,Ce,Pr,Nd			30mM KOH, 15mM HIA, 0.05% PVA	5.5	10mM BALA	CON	??	??		[72]
La,Ce,Pr,Nd,Sm, Eu, Gd,Tb,Dy,Ho, Er,Tm,Yb,Lu	Y		20mM NH_4OH, 7.5mM HIBA, 10mM malic acid, 0.1% HPC	4.8 (2-ethylbutyric acid)	20mM Car Hydro, 0.1% HPC	NON CON	2.5-200ppm	750s		[72,150]
Lu,Yb,Tm,Er,Ho, Dy,Tb,Gd,Eu,Sm , Pr,Ce,La			10mM HCl, 45% acetone		5mM EDTA	POT	??	1500s		[72,151]
Lanthanides ions			10mM KOH or NH_4OH, 4mM HIBA	4.8 (HAc)	10mM Car Hydro or EACA	PIXE	??	??		[89]

13.6 **Inorganic Anions – containing carbon (C)**

Ions analysed	Other ions detected	Interfering ions	LE	pH	TE	Detector	Concentration range	Time of analysis	Sample preparation	Ref
CO_3^{2-}	Br^-,I^-,SO_4^{2-}, Cl^-		10mM $Cd(NO_3)_2$		10mM CITR	POT	10mM	300s		[70–72,158]
H_2CO_3			5mM HCl	8.5 (Tris)	10mM NaAc	POT	Up to 40ppm	??		[159]
CO_3^{2-}	NO_3^-,AsO_4^{3-},AsO_3^{3-}		8mM HCl, 10mM α-CD, 1mg/ml HEC	9.0 (Tris)	10mM glycine (pH 9.0 by $Ba(OH)_2$)	CON	20mg/l	900s		[68,160]
CO_3^{2-},HCO_3^-			10mM HCl, 20m His	5.58	10mM MES	NON CON, UV (254nm)	??	1200s		[106]
CO_3^{2-}	PO_4^{3-}, organic acids		10mM HCl	7.2 (imidazole)	5mM disodium tetraborate	CON CON	0.025-0.5mM	1100s		[95]
HCO_3^-	PO_4^{3-},NO_3^-,NO_2^-,Cl^- ,SO_4^{2-}, SO_3^{2-}		PRE-SEPARATION: 8mM NaCl, 3mM BTP, 1.5mM BALA, 0.1% HEC ANALYTICAL: 1mM NaCl, 1.5mM BALA, 0.1% HEC		5mM CITR	CON	50-350µg/l	??		[93,148]

13.7 **Inorganic Anions – containing nitrogen (N)**

Ions analysed	Other ions detected	Interfering ions	LE	pH	TE	Detector	Concentration range	Time of analysis	Sample preparation	Ref
NO_3^-	Cl^-,SO_4^{2-}		6.25mM HBr, 1.25mM $InBr_3$, 1g/l HEC	3.15 (glycylglycine)	20mM CAA	NON CON, UV	0-20mg/l	400s		[161]
NO_3^-	F^-,SO_4^{2-}, Cl^-		10mM HCl, 3mM BTP, 1mg/l HEC	3.6 (glycylglycine)	TE=LE	CON	10mM	450s		[68,83]
NO_3^-	CrO_4^{2-},SO_4^{2-}, Cl^-		5mM $Ca(OH)_2$		10mM formic acid	CON CON	0.2-4mM	300s		[70–72,102]
NO_3^-	SO_4^{2-}		10mM $MgCl_2$, 0.2% HEC	6.0 (His)	5mM HAc (pH 5.0 by His)	CON	1-10ppm	150s		[71,162]
NO_3^-,NO_2^-	F^-,SO_4^{2-},PO_4^{3-}		PRE-SEPARATION: 8mM HCl, 0.1% HEC, 3mM BALA ANALYTICAL: 1mM HCl, 0.1% HEC	PS: 3.55 (BTP) AN: 3.55	2mM CITR	CON	0.2-100mg/l	200		[70,71,163]
NO_2^-	F^-,PO_4^{3-}		1mM HCl, 0.1% HEC	3.0	1mM CITR	CON	0.2-100mg/l	200s		[71,163]
NO_3^-	CO_3^{2-},AsO_4^{3-},AsO_3^{3-}		8mM HCl, 10mM α-CD, 1mg/ml HEC	9.0 (Tris)	10mM glycine (pH 9.0 by $Ba(OH)_2$)	CON	20mg/l	900s		[68,160]
NO_3^-,NO_2^-	$S_2O_3^{2-}$,SO_4^{2-},PO_4^3, $P_2O_7^{4-}$,F^-,I^-,Br^-,BrO_3^-, ClO_3^-,ClO_4^-,CrO_4^{2-}, AsO_4^{3-}, SCN^-,SeO_3^{2-}		10mMHCl, 0-10% PVA, 0.2% HEC	6.0 (His)	5mM MES (pH 6.0 by His)	SPH, UV (254nm)	10mM	200s		[70,71,164]
NO_3^-,NO_2^-	Cl^-,F^-,SO_4^{2-},PO_4^{3-}, oxalate,formate		PRE-SEPARATION: 10mM HCl, 0.1% MHEC ANALYTICAL: 5mM HCl, 2mM BTP, 0.1% MHEC	PS: 3.1 (BALA) AN: 3.6 (BALA)	5mM HAc	CON, UV	1-6μM	1200s		[165]
NO_3^-	SO_4^{2-}, Cl^-		8mM HCl, 3mM BTP, 0.1% HEC	3.5 (BALA)	2mM CITR	CON, UV	5-100ppm	500s		[166]
NO_3^-	SO_4^{2-}, Cl^-		8mM HCl, 3mM BTP, 0.2% HEC	3.4 (BALA)	3mM CITR	CON, UV	5-100ppm	500s		[166]
NO_3^-	SO_4^{2-},Cl^-		10mM HCl, 0.1% HEC	7.5 (Tris)	10mM MES (pH 6.0 by Tris)	CON, UV	5-100ppm	500s		[166]
NO_3^-,NO_2^-	SO_4^{2-},PO_4^{3-}		8mM HCl, 3.5mM BALA, 3mM BTP0.1% MHEC	3.55	5mM CITR	CON	??	1500s		[70,167]

NO_3^-,NO_2^-	SCN^-		5mM HCl, 1mM $CuCl_2$, 1g/l HEC	3.25 (glycylglycine)	20mM cyanoacetic acid	CON	5mg/l	300s		[168]
NO_3^-,NO_2^-	SCN^-		5mM HCl, 1mM $CuCl_2$, 1g/l HEC	6.0 (2-methylbenzimidazole)	20mM cyanoacetic acid	CON	10-20mg/l	250s		[168]
NO_3^-	SO_4^{2-}		10mM HCl	6.0 (His)	MES	CON	??	??		[169]
NO_3^-,NO_2^-	SO_4^{2-},PO_4^{3-},F^-,Cl^-		5mM dithionate, 1.8mM $MgCl_2$, 0.1% MHEC	3.5 (BALA)	5mM CITR	CON	0.4mM	350s		[68,170]
NO_3^-	F^-		10mM HCl, 0.1% HEC	3.6 (glycylglycine)	10mM benzoic acid	CON	10-50pm	150s		[68,123]
NO_3^-,NO_2^-	SO_4^{2-},PO_4^{3-},F^-,Cl^-		PRE-SEPARATION: 8mM HCl, 3.8mM BTP, 1.5mM BALA, 0.1% HEC ANALYTICAL: 2mM HCl, 1.5mM BALA, 0.1% HEC		5mM CITR	CON	1-125mg/l	Up to 1800s		[171]
NO_3^-,NO_2^-	$H_2PO_4^-$, SO_4^{2-}		10mM HCl, 2.5mM $MgCl_2$, 0.2% HEC	3.5 (BALA)	5mM CITR	CON	0.05-2mM	Up to 1800s		[72,73]
NO_3^-	SO_4^{2-}		2mM His-HCl, 2mM His, 3mM $CaCl_2$, 0.1% HPMC		10mM ammonium formate	CON	??	Up to 1200s		[135]
NO_2^-	F^-,Se(IV),Se(VI), SO_4^{2-}, SO_3^{2-}		5mM HCl, 1mg/ml HEC	4.1 (GABA)	10mM CITR	CON	4-16mg/l	350s		[140]
NO_3^-,NO_2^-	PO_4^{3-},Cl^-,SO_4^{2-},HCO_3^-, SO_3^{2-}		PRE-SEPARATION: 8mM NaCl, 3mM BTP, 1.5mM BALA, 0.1% HEC ANALYTICAL: 1mM NaCl, 1.5mM BALA, 0.1% HEC		5mM CITR	CON	50-350µg/l	??		[93,148]
NO_3^-,NO_2^-	SO_4^{2-},SO_3^{2-}		10mM HCl, 10mM BALA, 3mM BTP, 0.1-0.5% HPMC	3.6	10mM CITR	CON	??	??		[70]
NO_3^-			8mM HCl, 3.5mM BALA, 3mM BTP, 0.1% HEC	3.55	5mM CITR	CON	??	??		[70]

NO_3^-,NO_2^-			5mM HCl-His, 0.01% Triton X-100, 0 or 25mM α-CD		10mM NaAc	POT	0.5-3.0mM	1200s		[172]
NO_3^-,NO_2^-	SO_4^{2-},$H_2PO_4^-$		10mM HCl, 2.5mM $MgCl_2$, 1g/l HEC	3.6 (BALA)	5mM CITR	CON	0.2mM	Up to 1800s		[72,173]
NO_3^-,NO_2^-	SO_4^{2-},$H_2PO_4^-$		10mM HCl, 2.5mM $CaCl_2$, 1g/l HEC	3.6 (BALA)	5mM CITR	CON	0.2mM	Up to 1800s		[72,173]
NO_3^-,NO_2^-	SO_4^{2-},$H_2PO_4^-$		10mM HCl, 2.5mM BTP, 1g/l HEC	3.6 (BALA)	5mM CITR	CON	0.2mM	Up to 1800s		[72,173]
NO_3^-,NO_2^-	SO_4^{2-},$H_2PO_4^-$		10mM HCl, 2.5mM $MgCl_2$, 1g/l HEC	2.9 (Gly)	5mM CITR	CON	0.2mM	Up to 1800s		[72,173]
NO_3^-,NO_2^-	SO_4^{2-},$H_2PO_4^-$		10mM HCl, 2.5mM $CaCl_2$, 1g/l HEC	2.9 (Gly)	5mM CITR	CON	0.2mM	Up to 1800s		[72,173]
NO_3^-,NO_2^-	SO_4^{2-},$H_2PO_4^-$		10mM HCl, 2.5mM BTP, 1g/l HEC	2.9 (Gly)	5mM CITR	CON	0.2mM	Up to 1800s		[72,173]

13.8 **Inorganic Anions – containing phosphorus (P)**

Ions analysed	Other ions detected	Interfering ions	LE	pH	TE	Detector	Concentration range	Time of analysis	Sample preparation	Ref
PO_4^{3-}	Urate, hippurate		10mM HCl	5.5 (His)	10mM MES	CON	0.06-0.4mM	1500s		[174]
PO_4^{3-}	F^-,SO_4^{2-}, NO_3^-,NO_2^-		PRE-SEPARATION: 8mM HCl, 0.1% HEC, 3mM BALA ANALYTICAL: 1mM HCl, 0.1% HEC	PS: 3.55 (BTP) AN: 3.55	2mM CITR		0.2-100mg/l			[70,71,163]
PO_4^{3-}	NO_2^-,F^-		1mM HCl, 0.1% HEC	3.0	1mM CITR	CON	0.2-100mg/l	200s		[71,163]
PO_4^{3-},$P_2O_7^{4-}$	$S_2O_3^{2-}$,SO_4^{2-},NO_3^-, NO_2^-,F^-,I^-,Br^-,BrO_3^-, ClO_3^-,ClO_4^-,CrO_4^{2-}, AsO_4^{3-}, SCN^-,SeO_3^{2-}		10mMHCl, 0-10% PVA, 0.2% HEC	6.0 (His)	5mM MES (pH 6.0 by His)	SPH, UV (254nm)	10mM	200s		[70,71,164]
PO_4^{3-}	Cl^-,F^-,SO_4^{2-},NO_3^-, NO_2,oxalate, formate		PRE-SEPARATION: 10mM HCl, 0.1% MHEC ANALYTICAL: 5mM HCl, 2mM BTP, 0.1% MHEC	PS: 3.1 (BALA) AN: 3.6 (BALA)	5mM HAc	CON, UV	1-6µM	1200s		[165]
PO_4^{3-}	SO_4^{2-}, NO_3^-,NO_2^-		8mM HCl, 3.5mM BALA, 3mM BTP0.1% MHEC	3.55	5mM CITR	CON	??	1500s		[70,167]
PO_4^{3-},$P_2O_7^{4-}$,$P_3O_{10}^{5-}$, $P_3O_9^{3-}$			10mM HCl, 0.1% HEC	3.6 (BALA)	10mM CITR	CON	10mM	??		[175]
PO_4^{3-},$P_2O_7^{4-}$,$P_3O_{10}^{5-}$, $P_3O_9^{3-}$			10mM HCl, 3mM BTP, 0.1% HEC	3.6 (BALA)	10mM CITR	CON	10mM	??		[175]
PO_4^{3-},$P_2O_7^{4-}$,$P_3O_{10}^{5-}$, $P_3O_9^{3-}$			10mM HCl, 20mM glycylglycine	3.0	10mM CITR	CON	10mM	??		[175]
PO_4^{3-},$P_2O_7^{4-}$,$P_3O_{10}^{5-}$, $P_3O_9^{3-}$			10mM HCl	3.0 (glycine)	10mM CITR	CON	10mM	??		[175]

PO_4^{3-},$P_2O_7^{4-}$,$P_3O_{10}^{5-}$, $P_3O_9^{3-}$			5mM HCl	4.5 (BALA)	10mM CITR	CON	10mM	??		[175]
PO_4^{3-}	Acetate,lactate,EtG		10mM HCl, 0.2% HPC	4.4 (EACA)	10mM nicotinic acid, 0.2% HPC, (pH4.4 by EACA)	CON	0.5-50mM	400s		[176]
PO_4^{3-}	SO_4^{2-},organic acids		10mM HCl, 0.05% Mowiol, 0.2% HEC	2.9 (BALA)	5mM propionic acid (pH 7 by NaOH)	CON, UV (254nm)	Over 0.1mM	250s		[70,97]
PO_4^{3-}	Organicvacids, codeine		10mM HCl, 0.2% HEC	6.0 (His)	5mM MES	CON, UV (254nm)	0-4nM	900s		[177]
PO_4^{3-}	Organic acids, codeine		10mM KOH, 0.05% Mowiol	5.0 (HAc)	5mM HCl	CON, UV (254nm)	0-4nM	900s		[177]
PO_4^{3-}	Organic acids, codeine		10mM KOH, 0.05% Mowiol	5.0 (HIBA) then 4.2 (HAc)	5mM HCl	CON, UV (254nm)	0-4nM	900s		[177]
PO_4^{3-},PO_3^{3-}	Br^r,ClO_3^-,organic acids		6.6mM HCl	4.2 (aniline)	1.2mM HAc	NON CON, UV	0.8-2mM	300s		[178]
PO_4^{3-}	SO_4^{2-},organic acids		10mM HCl, 0.2% HEC	6.0 (His)	5mM MES	CON	??	600s		[179]
PO_4^{3-}	Organic acids		10mM HCl, 5.6mM BTP	6.1	5mM caproic acid	CON CON, UV (254nm)	0.05-2.5mM	Up to 1800s		[70,80,180]
PO_4^{3-}	Organic acids		20mM HCl, 30mM Gly, 5-25mM β-CD	2.5	5mM caproic acid	CON CON, UV (254nm)	0.05-2.5mM	Up to 1800s		[70,80,180]
PO_4^{3-}	SO_4^{2-}, Cl^-, organic acids		2mM HNO_3, 3mM $Cd(NO_3)_2$, 1.5mM BALA, 0.04% HPMC	3.0	20mM caproic acid or benzoic acid	POT, UV	0-40nM	1800s		[71,181]
Phosphorous oxoacids			10mM HCl, 0.1% Triton X-100	4.5-6.0 (His)	Hexanoic acid	POT	0.5-3.5μg/l	900s		[182]
PO_4^{3-}	Organic acids		10mM HCl	6.0 (His)	10mM caproic acid	CON, UV (254nm)	??	??		[183]
PO_4^{3-}	NO_3^-,NO_2^-,SO_4^{2-},F^-, Cl^-		5mM dithionate, 1.8mM $MgCl_2$, 0.1% MHEC	3.5 (BALA)	5mM CITR	CON	0.4mM	350s		[68,170]

PO_4^{3-}	SO_3^{2-},organic acids		10mM HCl, 0.1% MHEC	2.9 (BALA)	5mM glutamate or capronate (pH 5.0 by His)	CON	600-2100mg/l	850s		[68,184]
PO_4^{3-}	SO_4^{2-},NO_3^-,NO_2^-,F^-, Cl^-		PRE-SEPARATION: 8mM HCl, 3.8mM BTP, 1.5mM BALA, 0.1% HEC ANALYTICAL: 2mM HCl, 1.5mM BALA, 0.1% HEC		5mM CITR	CON	1-125mg/l	Up to 1800s		[171]
$H_2PO_4^-$	SO_4^{2-} ,NO_3^-,NO_2^-		10mM HCl, 2.5mM $MgCl_2$, 0.2% HEC	3.5 (BALA)	5mM CITR	CON	0.05-2mM	Up to 1800s		[72,73]
PO_4^{3-}	SO_4^{2-}, F^-		10mM HCl, 2mM TETA, 0.1% HEC	5.6 (His)	Caproic acid	CON	0.3-0.5g/l	??		[134]
PO_4^{3-}	organic acids		10mM HCl, 0.1% HEC	5.5 (His)	10mM hexanoic acid	CON CON	0.025-0.5mM	1100s		[95]
PO_4^{3-}	NO_3^-,NO_2^-,Cl^-,SO_4^{2-}, HCO_3^-,SO_3^{2-}		PRE-SEPARATION: 8mM NaCl, 3mM BTP, 1.5mM BALA, 0.1% HEC ANALYTICAL: 1mM NaCl, 1.5mM BALA, 0.1% HEC		5mM CITR	CON	50-350μg/l	??		[93,148]
PO_4^{3-}	SO_4^{2-},organic acids		10mM HCl, 0.2% Mowiol	6.0 (BTP)	5mM caprylic acid (pH 8.0 by Tris)	CON	??	??		[70]
PO_4^{3-}	Organic acids		5mM HCl	2.8 (Gly)	5mM caproic acid	CON	??	??		[70]
$H_2PO_4^-$	SO_4^{2-}, NO_3^-,NO_2^-		10mM HCl, 2.5mM $MgCl_2$, 1g/l HEC	3.6 (BALA)	5mM CITR	CON	0.2mM	Up to 1800s		[72,173]
$H_2PO_4^-$	SO_4^{2-}, NO_3^-,NO_2^-		10mM HCl, 2.5mM $CaCl_2$, 1g/l HEC	3.6 (BALA)	5mM CITR	CON	0.2mM	Up to 1800s		[72,173]
$H_2PO_4^-$	SO_4^{2-}, NO_3^-,NO_2^-		10mM HCl, 2.5mM BTP, 1g/l HEC	3.6 (BALA)	5mM CITR	CON	0.2mM	Up to 1800s		[72,173]
$H_2PO_4^-$	SO_4^{2-}, NO_3^-,NO_2^-		10mM HCl, 2.5mM $MgCl_2$, 1g/l HEC	2.9 (Gly)	5mM CITR	CON	0.2mM	Up to 1800s		[72,173]
$H_2PO_4^-$	SO_4^{2-}, NO_3^-,NO_2^-		10mM HCl, 2.5mM $CaCl_2$, 1g/l HEC	2.9 (Gly)	5mM CITR	CON	0.2mM	Up to 1800s		[72,173]

$H_2PO_4^-$	SO_4^{2-}, NO_3^-,NO_2^-		10mM HCl, 2.5mM BTP, 1g/l HEC	2.9 (Gly)	5mM CITR	CON	0.2mM	Up to 1800s		[72,173]
PO_4^{3-}	SO_4^{2-},fumaric acid		10mM HCl, 0.05% HPMC	3.0 (BALA)	10mM CITR	CON, UV (254nm)	25-1000ng/ml	500s		[185]
PO_4^{3-}	SO_4^{2-},fumaric acid, tartaric acid		10mM HCl, 5mM β-CD, 0.05% HPMC	3.0 (BALA)	10mM CITR	CON, UV (254nm)	25-1000ng/ml	500s		[185]
PO_4^{3-}	Orotic acid		100mM HCl, 14.5mM BALA, 0.2% HEC	3.25	5mM Asp	CON, PHO (218nm, 280nm)	5nM	200s??		[27]
PO_4^{3-}	Orotic acid		100mM HCl, 14.5mM BALA, 30mM α-CD, 0.2% HEC	3.25	5mM Asp	CON, PHO (218nm, 280nm)	5nM	200s??		[27]

13.9 **Inorganic Anions – containing sulphur (S)**

Ions analysed	Other ions detected	Interfering ions	LE	pH	TE	Detector	Concentration range	Time of analysis	Sample preparation	Ref
SO_4^{2-}	Al,Fe(III)-EDCTA complexes, F^-,Cl^-		10mM HCl, 0.1% HEC	5.7 (His)	MES	CON	0.3-0.5g/l	150s		[71,134]
SO_4^{2-}	Cr(VI),Se(VI),Se(IV), As(V)		20mM HNO_3, 0.5g/l Mowiol	5.5 (His)	20mM gallic acid	CON	10-20ppm	650s		[144]
SO_4^{2-}	I^-,Br^-,SO_4^{2-}, Cl^-		1.5-12mM HNO_3, 0-4mM $In(NO_3)_3$, 1g/l HEC	3.0 (glycylglycine)	20mM CAA	CON	10-100mg/l	600s		[68,186–188]
SO_4^{2-}	Cl^-,NO_3^-		6.25mM HBr, 1.25mM $InBr_3$, 1g/l HEC	3.15 (glycylglycine)	20mM CAA	NON CON, UV	0-20mg/l	400s		[161]
SO_4^{2-}	F^-,NO_3^-, Cl^-		10mM HCl, 3mM BTP, 1mg/l HEC	3.6 (glycylglycine)	TE=LE	CON	10mM	450s		[68,83]
HS^-,SO_3^{2-}			5mM NaOH, 0.1% HPMC		10mM NaAc	POT	Up to 2mg/l	1500s		[71,189]
HS^-,SO_3^{2-}			5mM HCl, 0.1% HPMC	10.5 (2-amino-2-methyl-1-propanol)	10mM NaAc	POT	Up to 2mg/l	1500s		[71,189]
HS^-,SO_3^{2-}			5mM NaOH		10mM NaAc	POT	Up to 2mg/l	1500s		[71,189]
SO_4^{2-}	CrO_4^{2-}, NO_3^-,Cl^-		5mM $Ca(OH)_2$		10mM formic acid	CON CON	0.2-4mM	300s		[70–72,102]
SO_4^{2-}	Br^-,I^-, Cl^-,CO_3^{2-}		10mM $Cd(NO_3)_2$		10mM CITR	POT	10mM	300s		[70–72,158]
SO_4^{2-}, SO_3^{2-} ,$S_2O_3^{2-}$			5mM HCl, 10mM His, (sol:50% acetone)		10mM CH_3COONa	POT	Up to 0.15nM	1500s		[71,190]
SO_4^{2-}	NO_3^-		10mM $MgCl_2$, 0.2% HEC	6.0 (His)	5mM HAc (pH 5.0 by His)	CON	1-10ppm	150s		[71,162]
SO_4^{2-}	F^-,NO_3^-,NO_2^-,PO_4^{3-}		PRE-SEPARATION: 8mM HCl, 0.1% HEC, 3mM BALA ANALYTICAL: 1mM HCl, 0.1% HEC	PS: 3.55 (BTP) AN: 3.55	2mM CITR	CON	0.2-100mg/l	200s		[70,71,163]
$S_2O_3^{2-}$,SO_4^{2-}	NO_3^-,NO_2^-,PO_4^{3-}, $P_2O_7^{4-}$,F^-,I^-,Br^-,BrO_3^-,		10mM HCl, 0-10% PVA, 0.2% HEC	6.0 (His)	5mM MES (pH 6.0 by His)	SPH, UV (254nm)	10mM	200s		[70,71,164]

	ClO_3^-,ClO_4^-,CrO_4^{2-}, AsO_4^{3-}, SCN^-,SeO_3^{2-}									
SO_4^{2-}	Cl^-,F^-,PO_4^{3-},NO_3^-, NO_2,oxalate, formate		PRE-SEPARATION: 10mM HCl, 0.1% MHEC ANALYTICAL: 5mM HCl, 2mM BTP, 0.1% MHEC	PS: 3.1 (BALA) AN: 3.6 (BALA)	5mM HAc	CON, UV	1-6μM	1200s		[165]
SO_4^{2-}	NO_3^-, Cl^-		8mM HCl, 3mM BTP, 0.1% HEC	3.5 (BALA)	2mM CITR	CON, UV	5-100ppm	500s		[166]
SO_4^{2-}	NO_3^-, Cl^-		8mM HCl, 3mM BTP, 0.2% HEC	3.4 (BALA)	3mM CITR	CON, UV	5-100ppm	500s		[166]
SO_4^{2-}	NO_3^-, Cl^-		10mM HCl, 0.1% HEC	7.5 (Tris)	10mM MES (pH 6.0 by Tris)	CON, UV	5-100ppm	500s		[166]
SO_4^{2-}	PO_4^{3-},NO_3^-,NO_2^-		8mM HCl, 3.5mM BALA, 3mM BTP0.1% MHEC	3.55	5mM CITR	CON	??	1500s		[70,191]
SO_4^{2-}	PO_4^{3-},organic acids		10mM HCl, 0.05% Mowiol, 0.2% HEC	2.9 (BALA)	5mM propionic acid (pH 7 by NaOH)	CON, UV (254nm)	Over 0.1mM	250s		[70,97]
SO_4^{2-}	F^-,Cl^-		6mM $Cd(NO_3)_2$		10mM CITR	??	1ppm	1200s		[71,192]
SO_4^{2-}	F^-,Cl^-		10mM HCl, 0.1% Triton X-100	4.0 (His)	10mM hexanoic acid	??	1ppm	1200s		[71,192]
SO_4^{2-}	PO_4^{3-}, organic acids		10mM HCl, 0.2% HEC	6.0 (His)	5mM MES	CON	??	600s		[178]
SO_4^{2-}	Cl^-		5mM $Cd(NO_3)_2$, 20-40% acetone		5mM hexanoic acid	??	??	1200s		[71,193]
SO_4^{2-}	Cl^-		5mM $Cd(NO_3)_2$, 20-40% C_2H_5OH		5mM hexanoic acid	??	??	1200s		[71,193]
SO_4^{2-}	Cl^-		5mM $Ca(OH)_2$		5mM hexanoic acid	??	??	1200s		[71,193]
SO_4^{2-}, SO_3^{2-}			10mM HCl	4.0 (His)	10mM hexanoic acid	POT, UV (257nm)	0.2-12mM	1500s		[71,194]
SO_4^{2-}	PO_4^{3-},Cl^-, organic acids		2mM HNO_3, 3mM $Cd(NO_3)_2$, 1.5mM BALA, 0.04% HPMC	3.0	20mM caproic acid or benzoic acid	POT, UV	0-40nM	1800s		[71,181]
SO_4^{2-}	Cl^-		8mM $Cd(NO_3)_2$		5mM CITR	THE, UV	??	??		[71,195]

SO_4^{2-}	NO_3^-		10mM HCl	6.0 (His)	MES	CON	??	??		[169]
SO_4^{2-}	Cl^-, CrO_4^{2-}, organic acids		10mM His, 10mM HCl-His		10mM phenyl acetate	CON	??	500s		[110]
SO_4^{2-}	Cl^-		10mM HCl	2.9 (BALA)	10mM CITR	CPN, UV (254nm)	??	??		[183]
SO_4^{2-}	NO_3^-,NO_2^-, PO_4^{3-}, F^-, Cl^-		5mM dithionate, 1.8mM $MgCl_2$, 0.1% MHEC	3.5 (BALA)	5mM CITR	CON	0.4mM	350s		[68,196]
SO_3^{2-}	organic acids, PO_4^{3-}		10mM HCl, 0.1% MHEC	2.9 (BALA)	5mM glutamate or capronate (pH 5.0 by His)	CON	600-2100mg/l	850s		[68,184]
SO_4^{2-}	PO_4^{3-},NO_3^-,NO_2^-,F^-, Cl^-		PRE-SEPARATION: 8mM HCl, 3.8mM BTP, 1.5mM BALA, 0.1% HEC ANALYTICAL: 2mM HCl, 1.5mM BALA, 0.1% HEC		5mM CITR	CON	1-125mg/l	Up to 1800s		[171]
SO_4^{2-}	Cl^-		10mM HCl, 4mM BALA, 4mM BTP, 0.05% MHEC	3.5	20mM CITR, 30mM BALA, 0.05% MHEC	CON	0.6-7.2mg/l	700s		[68,197]
SO_3^{2-}			10mM HCl, 0.05% MHEC	3.0 (BALA)	20mM tartrate, 0.05% MHEC (pH 3.9 by BALA)	CON	2-23mg/l	350s		[68,198]
SO_4^{2-}	$H_2PO_4^-$,NO_3^-,NO_2^-		10mM HCl, 2.5mM $MgCl_2$, 0.2% HEC	3.5 (BALA)	5mM CITR	CON	0.05-2mM	Up to 1800s		[72,73]
SO_4^{2-}	PO_4^{3-}, F^-		10mM HCl, 2mM TETA, 0.1% HEC	5.6 (His)	Caproic acid	CON	0.3-0.5g/l	??		[134]
SO_4^{2-}, SO_3^{2-}	NO_2^-,F^-,Se(IV), Se(VI)		5mM HCl, 1mg/ml HEC	4.1 (GABA)	10mM CITR	CON	4-16mg/l	350s		[140]
SO_4^{2-},SO_3^{2-}	NO_3^-,NO_2^-,Cl^-,PO_4^{3-}, HCO_3^-		PRE-SEPARATION: 8mM NaCl, 3mM BTP, 1.5mM BALA, 0.1% HEC ANALYTICAL: 1mM NaCl, 1.5mM BALA, 0.1% HEC		5mM CITR	CON	50-350μg/l	??		[93,148]

SO_4^{2-},SO_3^{2-}	NO_3^-,NO_2^-		10mM HCl, 10mM BALA, 3mM BTP, 01.05% HPMC	3.6	10mM CITR	CON	??	??		[70]
SO_4^{2-}	PO_4^{3-}, organic acids		10mM HCl, 0.2% Mowiol	6.0 (BTP)	5mM caprylic acid (pH 8.0 by Tris)	CON	??	??		[70]
SO_4^{2-}	NO_3^-,NO_2^-, $H_2PO_4^-$		10mM HCl, 2.5mM $MgCl_2$, 1g/l HEC	3.6 (BALA)	5mM CITR	CON	0.2mM	Up to 1800s		[72,173]
SO_4^{2-}	NO_3^-,NO_2^-, $H_2PO_4^-$		10mM HCl, 2.5mM $CaCl_2$, 1g/l HEC	3.6 (BALA)	5mM CITR	CON	0.2mM	Up to 1800s		[72,173]
SO_4^{2-}	NO_3^-,NO_2^-, $H_2PO_4^-$		10mM HCl, 2.5mM BTP, 1g/l HEC	3.6 (BALA)	5mM CITR	CON	0.2mM	Up to 1800s		[72,173]
SO_4^{2-}	NO_3^-,NO_2^-, $H_2PO_4^-$		10mM HCl, 2.5mM $MgCl_2$, 1g/l HEC	2.9 (Gly)	5mM CITR	CON	0.2mM	Up to 1800s		[72,173]
SO_4^{2-}	NO_3^-,NO_2^-, $H_2PO_4^-$		10mM HCl, 2.5mM $CaCl_2$, 1g/l HEC	2.9 (Gly)	5mM CITR	CON	0.2mM	Up to 1800s		[72,173]
SO_4^{2-}	NO_3^-,NO_2^-, $H_2PO_4^-$		10mM HCl, 2.5mM BTP, 1g/l HEC	2.9 (Gly)	5mM CITR	CON	0.2mM	Up to 1800s		[72,173]
SO_4^{2-}	PO_4^{3-},fumaric acid		10mM HCl, 0.05% HPMC	3.0 (BALA)	10mM CITR	CON, UV (254nm)	25-1000ng/ml	500s		[185]
SO_4^{2-}	PO_4^{3-},fumaric acid, tartaric acid		10mM HCl, 5mM β-CD, 0.05% HPMC	3.0 (BALA)	10mM CITR	CON, UV (254nm)	25-1000ng/ml	500s		[185]

13.10 **Inorganic Anions – containing fluorine (F)**

Ions analysed	Other ions detected	Interfering ions	LE	pH	TE	Detector	Concentration range	Time of analysis	Sample preparation	Ref
F^-	Al,Fe(III)-EDCTA complexes,SO_4^{2-}, Cl^-		10mM HCl, 0.1% HEC	5.7 (His)	MES	CON	0.3-0.5g/l	150s		[71,134]
F^-	Cl^-,NO_3^-,SO_4^{2-}		10mM HCl, 3mM BTP, 1mg/l HEC	3.6 (glycylglycine)	TE=LE	CON	10mM	450s		[68,83]
F^-	PO_4^{3-},SO_4^{2-},NO_3^-, NO_2^-		PRE-SEPARATION: 8mM HCl, 0.1% HEC, 3mM BALA ANALYTICAL: 1mM HCl, 0.1% HEC	PS: 3.55 (BTP) AN: 3.55	2mM CITR	CON	0.2-100mg/l	200s		[70,71,163]
F^-	PO_4^{3-},NO_2^-		1mM HCl, 0.1% HEC	3.0	1mM CITR	CON	0.2-100mg/l	200s		[71,163]
F^-	$S_2O_3^{2-}$,SO_4^{2-},NO_3^-, NO_2^-,PO_4^{3-},$P_2O_7^{4-}$,I^-, Br^-,BrO_3^-,ClO_3^-, ClO_4^-,CrO_4^{2-},AsO_4^{3-}, SCN^-,SeO_3^{2-}		10mMHCl, 0-10% PVA, 0.2% HEC	6.0 (His)	5mM MES (pH 6.0 by His)	SPH, UV (254nm)	10mM	200s		[70,71,164]
F^-	Cl^-,SO_4^{2-},PO_4^{3-},NO_3^-, NO_2,oxalate, formate		PRE-SEPARATION: 10mM HCl, 0.1% MHEC ANALYTICAL: 5mM HCl, 2mM BTP, 0.1% MHEC	PS: 3.1 (BALA) AN: 3.6 (BALA)	5mM HAc	CON, UV	1-6μM	1200s		[165]
F^-			PRE-SEPARATION: 8mM HCl, 22mM EACA, 1mM $CaCl_2$, 0.05% HPMC ANALYTICAL: 2mM HCl, 5mM EACA, 0.05% HPMC		10mM tartaric acid	CON CON	0.2-1μg/ml	1700s		[70,80,199]
F^-			2mM HCl, 5mM EACA, 0.05% HPMC		2mM tartaric acid	CON CON		1700s		[70,72,199]
F^-	SO_4^{2-},Cl^-		6mM $Cd(NO_3)_2$		10mM CITR	??	1ppm	1200s		[71,192]
F^-	SO_4^{2-},Cl^-		10mM HCl, 0.1% Triton X-100	4.0 (His)	10mM hexanoic acid	??	1ppm	1200s		[71,192]

F^-	SO_4^{2-},NO_3^-,NO_2^-, PO_4^{3-}, Cl^-		5mM dithionate, 1.8mM $MgCl_2$, 0.1% MHEC	3.5 (BALA)	5mM CITR	CON	0.4mM	350s		[68,196]
F^-	NO_3^-		10mM HCl, 0.1% HEC	3.6 (glycylglycine)	10mM benzoic acid	CON	10-50pm	150s		[68,123]
F^-	PO_4^{3-},NO_3^-,NO_2^-, SO_4^{2-} ,Cl^-		PRE-SEPARATION: 8mM HCl, 3.8mM BTP, 1.5mM BALA, 0.1% HEC ANALYTICAL: 2mM HCl, 1.5mM BALA, 0.1% HEC		5mM CITR	CON	1-125mg/l	Up to 1800s		[171]
F^-	PO_4^{3-},SO_4^{2-}		10mM HCl, 2mM TETA, 0.1% HEC	5.6 (His)	Caproic acid	CON	0.3-0.5g/l	??		[134]
F^-	NO_2^-,Se(IV), Se(VI), SO_4^{2-}, SO_3^{2-}		5mM HCl, 1mg/ml HEC	4.1 (GABA)	10mM CITR	CON	4-16mg/l	350s		[140]
F^-	Cl^-,Br^-,caproate		10mM KI (sol: CH_3OH)		10mM palmitic acid (sol: CH_3OH)	POT, CON	??	1500s		[107]

13.11 Inorganic Anions – containing chlorine (Cl)

Ions analysed	Other ions detected	Interfering ions	LE	pH	TE	Detector	Concentration range	Time of analysis	Sample preparation	Ref
Cl^-	Al,Fe(III)-EDCTA complexes,SO_4^{2-},F^-,		10mM HCl, 0.1% HEC	5.7 (His)	MES	CON	0.3-0.5g/l	150s		[71,134]
Cl^-,ClO_4^- ,ClO_3^-			1.75mM HNO_3, 2.75mM $In(NO_3)_3$, 9mM α-CD, 1g/l HEC	3.0 (glycylglycine)	20mM CAA	CON	5-20ppm	400s		[200]
Cl^-	I^-,Br^-,SO_4^{2-}		1.5-12mM HNO_3, 0-4mM $In(NO_3)_3$, 1g/l HEC	3.0 (glycylglycine)	20mM CAA	CON	10-100mg/l	600s		[68,186–188]
Cl^-	NO_3^-,SO_4^{2-}		6.25mM HBr, 1.25mM $InBr_3$, 1g/l HEC	3.15 (glycylglycine)	20mM CAA	NON CON, UV	0-20mg/l	400s		[161]
Cl^-	F^-,NO_3^-,SO_4^{2-}		10mM HCl, 3mM BTP, 1mg/l HEC	3.6 (glycylglycine)	TE=LE	CON	10mM	450s		[68,83]
Cl^-	CrO_4^{2-}, NO_3^-, SO_4^{2-}		5mM $Ca(OH)_2$		10mM formic acid	CON CON	0.2-4mM	300s		[70–72,102]
Cl^-	Br^-,I^-,SO_4^{2-},CO_3^{2-}		10mM $Cd(NO_3)_2$		10mM CITR	POT	10mM	300s		[70–72,158]
ClO_3^-, ClO_4^-	$S_2O_3^{2-}$,SO_4^{2-},NO_3^-, NO_2^-,PO_4^{3-},$P_2O_7^{4-}$,I^-, F^-,Br^-,BrO_3^-,CrO_4^{2-}, AsO_4^{3-}, SCN^-,SeO_3^{2-}		10mM HCl, 0-10% PVA, 0.2% HEC	6.0 (His)	5mM MES (pH 6.0 by His)	SPH, UV (254nm)	10mM	200s		[70,71,164]
Cl^-	F^-,SO_4^{2-},PO_4^{3-},NO_3^-, NO_2,oxalate, formate		PRE-SEPARATION: 10mM HCl, 0.1% MHEC ANALYTICAL: 5mM HCl, 2mM BTP, 0.1% MHEC	PS: 3.1 (BALA) AN: 3.6 (BALA)	5mM HAc	CON, UV	1-6μM	1200s		[165]
Cl^-	SO_4^{2-},NO_3^-		8mM HCl, 3mM BTP, 0.1% HEC	3.5 (BALA)	2mM CITR	CON, UV	5-100ppm	500s		[166]
Cl^-	SO_4^{2-},NO_3^-		8mM HCl, 3mM BTP, 0.2% HEC	3.4 (BALA)	3mM CITR	CON, UV	5-100ppm	500s		[166]
Cl^-	SO_4^{2-},NO_3^-		10mM HCl, 0.1% HEC	7.5 (Tris)	10mM MES (pH 6.0 by Tris)	CON, UV	5-100ppm	500s		[166]
Cl^-	SO_4^{2-},F^-		6mM $Cd(NO_3)_2$		10mM CITR	??	1ppm	1200s		[71,192]
Cl^-	SO_4^{2-},F^-		10mM HCl, 0.1% Triton X-100	4.0 (His)	10mM hexanoic acid	??	1ppm	1200s		[71,192]

ClO_3^-	PO_4^{3-},PO_3^{3-},Br^-, organic acids		6.6mM HCl	4.2 (aniline)	1.2mM HAc	NON CON, UV	0.8-2mM	300s		[178]
Cl^-	SO_4^{2-}		5mM $Cd(NO_3)_2$, 20-40% acetone		5mM hexanoic acid	??	??	1200s		[71,193]
Cl^-	SO_4^{2-}		5mM $Cd(NO_3)_2$, 20-40% C_2H_5OH		5mM hexanoic acid	??	??	1200s		[71,193]
Cl^-	SO_4^{2-}		5mM $Ca(OH)_2$		5mM hexanoic acid	??	??	1200s		[71,193]
Cl^-	PO_4^{3-}, SO_4^{2-},organic acids		2mM HNO_3, 3mM $Cd(NO_3)_2$, 1.5mM BALA, 0.04% HPMC	3.0	20mM caproic acid or benzoic acid	POT, UV	0-40nM	1800s		[71,181]
Cl^-	SO_4^{2-}		8mM $Cd(NO_3)_2$		5mM CITR	THE, UV	??	??		[71,195]
Cl^-	SO_4^{2-}, CrO_4^{2-}, organic acids		10mM His, 10mM HCl-His		10mM phenyl acetate	CON	??	500s		[110]
Cl^-	SO_4^{2-}		10mM HCl	2.9 (BALA)	10mM CITR	CPN, UV (254nm)	??	??		[183]
Cl^-	SO_4^{2-},NO_3^-,NO_2^-, PO_4^{3-}, F^-		5mM dithionate, 1.8mM $MgCl_2$, 0.1% MHEC	3.5 (BALA)	5mM CITR	CON	0.4mM	350s		[68,196]
Cl^-	PO_4^{3-},NO_3^-,NO_2^-, SO_4^{2-} ,F^-		PRE-SEPARATION: 8mM HCl, 3.8mM BTP, 1.5mM BALA, 0.1% HEC ANALYTICAL: 2mM HCl, 1.5mM BALA, 0.1% HEC		5mM CITR	CON	1-125mg/l	Up to 1800s		[171]
Cl^-	SO_4^{2-}		10mM HCl, 4mM BALA, 4mM BTP, 0.05% MHEC	3.5	20mM CITR, 30mM BALA, 0.05% MHEC	CON	0.6-7.2mg/l	700s		[68,197]
Cl^-	F^-,Br^-,caproate		10mM KI (sol: CH_3OH)		10mM palmitic acid (sol: CH_3OH)	POT, CON	??	1500s		[107]
Cl^-	NO_3^-,NO_2^-,SO_4^{2-}, SO_3^{2-},PO_4^{3-},HCO_3^-		PRE-SEPARATION: 8mM NaCl, 3mM BTP, 1.5mM BALA, 0.1% HEC		5mM CITR	CON	50-350μg/l	??		[93,148]

			ANALYTICAL: 1mM NaCl, 1.5mM BALA, 0.1% HEC							
ClO_4^-, ClO_3^-			5mM HCl-His, 0.01% Triton X-100, 0 or 10mM α-CD		10mM NaAc	POT	0.5-3.0mM	1200s		[172]

13.12 Inorganic Anions – containing bromine (Br)

Ions analysed	Other ions detected	Interfering ions	LE	pH	TE	Detector	Concentration range	Time of analysis	Sample preparation	Ref
Br^-	Fe(II),Cr(III),Zr,Mo, Ru,Te		20mM NH_3, 1mM tartaric acid, 0.1% HPC	5.0 (HAc)	10mM Car Hydro	High-purity Ge detector, PIXE	Up to 50nM	500s		[91]
Br^-	I^-,Cl^-,SO_4^{2-}		1.5-12mM HNO_3, 0-4mM $In(NO_3)3$, 1g/l HEC	3.0 (glycylglycine)	20mM CAA	CON	10-100mg/l	600s		[68,186–188]
Br^-	I^-		5mM HCl, 1.5mM NR_4^+, 0.01% HPMC	5.0 (His)	10mM sodium hexanoate	POT	0.5-2.5mM	1200s		[71,80,201]
Br^-	Cl^-,I^-,SO_4^{2-},CO_3^{2-}		10mM $Cd(NO_3)_2$		10mM CITR	POT	10mM	300s		[70–72,158]
Br^-,BrO_3^-	$S_2O_3^{2-}$,SO_4^{2-},NO_3^-, NO_2^-,PO_4^{3-},$P_2O_7^{4-}$,I^-, ClO_3^-, ClO_4^-,F^-,CrO_4^{2-}, AsO_4^{3-}, SCN^-,SeO_3^{2-}		10mMHCl, 0-10% PVA, 0.2% HEC	6.0 (His)	5mM MES (pH 6.0 by His)	SPH, UV (254nm)	10mM	200s		[70,71,164]
Br^-	PO_4^{3-},PO_3^{3-}, ClO_3^-, organic acids		6.6mM HCl	4.2 (aniline)	1.2mM HAc	NON CON, UV	0.8-2mM	300s		[178]
BrO_3^-			10mM HCl, 0.05% MHEC	3.2 (BALA)	10mM aspartate, 0.1% MHEC (pH 4.2 by BALA)	CON	150-500nM	800s		[68,202]
Br^-	Cl^-,F^-,caproate		10mM KI (sol: CH_3OH)		10mM palmitic acid (sol: CH_3OH)	POT, CON	??	1500s		[107]

13.13 Inorganic Anions – containing iodine (I)

Ions analysed	Other ions detected	Interfering ions	LE	pH	TE	Detector	Concentration range	Time of analysis	Sample preparation	Ref
I^-	Cl^-,Br^-,SO_4^{2-}		1.5-12mM HNO_3, 0-4mM $In(NO_3)_3$, 1g/l HEC	3.0 (glycylglycine)	20mM CAA	CON	10-100mg/l	600s		[68,186–188]
I^-	Br^-		5mM HCl, 1.5mM NR_4^+, 0.01% HPMC	5.0 (His)	10mM sodium hexanoate	POT	0.5-2.5mM	1200s		[71,80,201]
I^-	Cl^-,Br^-,SO_4^{2-},CO_3^{2-}		10mM $Cd(NO_3)_2$		10mM CITR	POT	10mM	300s		[70–72,158]
I^-	$S_2O_3^{2-}$,SO_4^{2-},NO_3^-, NO_2^-,PO_4^{3-},$P_2O_7^{4-}$, ClO_3^-, ClO_4^-,F^-,CrO_4^{2-}, AsO_4^{3-},Br^-,BrO_3^-, SCN^-,SeO_3^{2-}		10mM HCl, 0-10% PVA, 0.2% HEC	6.0 (His)	5mM MES (pH 6.0 by His)	SPH, UV (254nm)	10mM	200s		[70,71,164]
IO_3^-, IO_4^-			PRE-SEPARATION & ANALYTICAL: 5mM HCl, 0.01% Triton X-100	PRE: 4.3 (His) ANA: 3.6 (BALA)	10mM NaAc	POT	1mM	1200s		[80,203]
I^-			5mM HCl-His, 0.01% Triton X-100, 0 or 20mM α-CD		10mM NaAc	POT	0.5-3.0mM	1020s		[172]

13.14 Inorganic Anions

Ions analysed	Other ions detected	Interfering ions	LE	pH	TE	Detector	Concentration range	Time of analysis	Sample preparation	Ref
Te	Fe(II),Cr(III),Zr,Mo, Ru, Br^-		20mM NH_3, 1mM tartaric acid, 0.1% HPC	5.0 (HAc)	10mM Car Hydro	High-purity Ge detector, PIXE	Up to 50nM	500s		[91]
AsO_4^{3-} ,AsO_3^{3-}	CO_3^{2-},NO_3^-,		8mM HCl, 10mM α-CD, 1mg/ml HEC	9.0 (Tris)	10mM glycine (pH 9.0 by $Ba(OH)_2$)	CON	20mg/l	900s		[68,160]
CrO_4^{2-} ,AsO_4^{3-},SCN^- ,SeO_3^{2-}	$S_2O_3^{2-}$,SO_4^{2-},NO_3^-, NO_2^-,PO_4^{3-},$P_2O_7^{4-}$, ClO_3^-,ClO_4^-,F^-,Br^-, BrO_3^-, I^-		10mM HCl, 0-10% PVA, 0.2% HEC	6.0 (His)	5mM MES (pH 6.0 by His)	SPH, UV (254nm)	10mM	200s		[70,71,164]
CrO_4^{2-}	Cl^-, NO_3^-, SO_4^{2-}		5mM $Ca(OH)_2$		10mM formic acid	CON CON	0.2-4mM	300s		[70–72,102]
SCN^-	NO_3^-,NO_2^-		5mM HCl, 1mM $CuCl_2$, 1g/l HEC	3.25 (glycylglycine)	20mM cyanoacetic acid	CON	5mg/l	300s		[168]
SCN^-	NO_3^-,NO_2^-		5mM HCl, 1mM $CuCl_2$, 1g/l HEC	6.0 (2-methylbenzimidazole)	20mM cyanoacetic acid	CON	10-20mg/l	250s		[168]
CrO_4^{2-}	SO_4^{2-}, Cl^-, organic acids		10mM His, 10mM HCl-His		10mM phenyl acetate	CON	??	500s		[110]
NCS^-,$NCSe^-$, OCN^-			5mM HCl-His, 0.01% Triton X-100, 0 or 45mM α-CD		10mM NaAc	POT	0.5-3.0mM	1200s		[172]

13.15 Other substances

Ions analysed	Other ions detected	Interfering ions	LE	pH	TE	Detector	Concentration range	Time of analysis	Sample preparation	Ref
triethylamine	Na,Ba,Mg,Sr		20mM KOH, 1mM CITR	5.0	10mM $MgCl_2$	CON	2.8mM	1200s		[71,128]
n-butylamine	Na		10mM KOH	5.5 (CITR)	10mM creatinine (pH 7.0 by HCl)	CON	130-150mM	??		[108]
thiamine	Na,Rb,Ca		10mM NH_4Pic, 30mM 18-c-6-e, 0.4% Triton X-100	5.4	5mM HAc	CON	0.02-0.12g/ml	400s		[71,109]
Amaranth dye	La,Dy		10mM HCl, 0.05% Mowiol	6.0 (His)	10mM MES (pH 6.0 by His)	CON	2.5mM, dye 10mM	400s		[157]
vitamin B_1, HFG	Na,Ca		PRE-SEPARATION: 10mM KOH, 0.2% Triton X-100 ANALYTICAL: 5mM KOH	PS: 6.0 (MES) AN: 5.7 (MES)	10mM EACA	CON, UV (254nm)	2mM	1000s		[111]
vitamin B_1	Na,K,Ca		PRE-SEPARATION: 5mM KOH, 0.2% Triton X-100 ANALYTICAL: 25mM EACA, 0.2% Triton X-100	PS: 5.7 (MES) AN: 4.0 (HAc)	25mM EACA, 0.2% Triton X-100, (pH 4.0 by HAc)	CON, UV (254nm)	??	1300s		[111]
ascorbate			5mM glycolic acid, 1g/l HEC	8.0 (Tris)	10mM glycylglycine (pH 8.5 by $Ba(OH)_2$)	CON	0.01-0.5mM	350s		[68,204]
Urate, hippurate	PO_4^{3-}		10mM HCl	5.5 (His)	10mM MES	CON	0.06-0.4mM	1500s		[174]
oxalate, formate	F^-,SO_4^{2}, PO_4^{3-},NO_3^-, NO_2^-, Cl^-		PRE-SEPARATION: 10mM HCl, 0.1% MHEC ANALYTICAL: 5mM HCl, 2mM BTP, 0.1% MHEC	PS: 3.1 (BALA) AN: 3.6 (BALA)	5mM HAc	CON,UV	1-6μM	1200s		[165]
Malic acid. Fumaric acid			10mM HCl, 12mM BALA, 0.05% HPMC		5mM HAc	CON,UV	1mM	1500s		[205]
His, creatinine			10mM NH_4OH, 20mM MES		10mM EACA, 5mM HAc	CON,UV	5mM	1500s		[205]

Acetates, citrates, phosphates, thiodiacetates			10mM HCl, 0.2% HPC	4.4 (BALA)	10mM HAc	CON	0-3nM	1200s		[206]
Acetates, citrates, phosphates, thiodiacetates			10mM HCl, 0.2% HPC	3.3 (HAc)	10mM HAc	CON	0-3nM	1h		[206]
Acetate,lactate,EtG	PO_4^{3-}		10mM HCl, 0.2% HPC	4.4 (EACA)	10mM nicotinic acid, 0.2% HPC, (pH4.4 by EACA)	CON	0.5-50mM	400s		[176]
Organic acids	PO_4^{3-}		10mM HCl, 5.6mM BTP	6.1	5mM caproic acid	CON CON, UV (254nm)	0.05-2.5mM	Up to 1800s		[70,80,180]
Organic acids	PO_4^{3-}		20mM HCl, 30mM Gly, 5-25mM β-CD	2.5	5mM caproic acid	CON CON, UV (254nm)	0.05-2.5mM	Up to 1800s		[70,80,180]
Organic acids			10mM HCl, 0.1% poly(vinylpyrrolidone)	2.9 (BALA)	10mM nicotinic acid	CON	0.008-0.1M	1200s		[207]
Organic acids			10mM HCl, 5.5mM Tris, 0.1% poly(vinylpyrrolidone)		5mM MES	CON	0.008-0.1M	1200s		[207]
Organic acids	PO_4^{3-},SO_4^{2-}, Cl^-		2mM HNO_3, 3mM $Cd(NO_3)_2$, 1.5mM BALA, 0.04% HPMC	3.0	20mM caproic acid or benzoic acid	POT, UV	0-40nM	1800s		[71,181]
CH_3COO^-			10mM HCl, 0.1% Triton X-100	6.0 (His)	5mM glutamic acid	THE, UV	0-50nM	??		[71,195]
Organic acids			HCl	3.0 (quinine)	Propionic acid	CON, UV (254nm)	??	??		[169]
Organic acids	SO_4^{2-},Cl^-, CrO_4^{2-}		10mM His, 10mM HCl-His		10mM phenyl acetate	CON	??	500s		[110]
ic acids	SO_3^{2-}, PO_4^{3-}		10mM HCl, 0.1% MHEC	2.9 (BALA)	5mM glutamate or capronate (pH 5.0 by His)	CON	600-2100mg/l	850s		[68,184]
Organic acids			10mM HCl, 0.05% Mowiol or 0.2% HEC	6.0 (His)	5mM MES	CON	Up to 5mM	500s		[208]

Organic acids			10mM HCl, 0.05% Mowiol or 0.2% HEC	6.0 (DME)	5mM MES	CON	Up to 5mM	500s		[208]
Organic acids			10mM HCl, 0.05% Mowiol or 0.2% HEC, 2mM DAP	6.0 (His)	5mM MES	CON	Up to 5mM	500s		[208]
Organic acids			10mM HCl, 0.05% Mowiol or 0.2% HEC, 2mM Ca^{2+}	6.0 (His)	5mM capronate	CON	Up to 5mM	500s		[208]
Organic acids			10mM HCl, 0.05% Mowiol or 0.2% HEC	6.0 (BTP)	5mM capronate	CON	Up to 5mM	500s		[208]
Organic acids			10mM HCl, 0.05% Mowiol or 0.2% HEC	6.0 (His)	5mM capronate	CON	Up to 5mM	500s		[208]
Organic acids			10mM HCl, 0.05% Mowiol or 0.2% HEC	6.0 (DME)	5mM capronate	CON	Up to 5mM	500s		[208]
Organic phosphates			10mM HCl, 0.2% HPMC	6.0 (His)	10mM MES (pH 6.0 by Tris)	CON	??	??		[209]
Organic acids			10mM HCl, 0.2% HEC	6.0 (His)	10mM MES (pH 6.0 by Tris)	CON, PHO (256nm)	0-12nM	300s		[210]
Organic acids			10mM HCl, 0.2% HEC	3.0 (BALA)	7mM Glutamate (pH 6.0 by His)	CON, PHO (256nm)	0-12nM	300s		[210]
Organic acids			10mM HCl, 0.2% HEC	3.0 (BALA)	HAc	CON	0-10nM	150s		[211]
Organic acids			10mM HCl, 0.2% HEC	4.5 (EACA)	Caproic acid	CON	0-10nM	150s		[211]
Organic acids			10mM HCl, 0.2% HEC	6.0 (His)	MES	CON	0-10nM	150s		[211]
Organic acids			10mM HCl, 0.2% HEC	6.0 (BTP)	MES	CON	0-10nM	150s		[211]
Organic acids			10mM HCl, 0.2% HEC, 2mM Ca^{2+}	6.0 (His)	MES	CON	0-10nM	150s		[211]
Fatty acids			5mM HCl, 0.1% HEC, (sol: 20% CH_3OH)	6.0 (His)	2.5mM MES, (sol: 30%CH_3OH)	CON, PHO (405nm)	Above 1nM	200s		[119]
Organic acids			1 or 10mM HCl, 0.2% HPMC	6.0 (His)	10mM MES (pH 6.0 by Tris)	CON, UV	100ng/l	200s		[212]
Creatinine, GABA,BALA			10mM KAc	4.7 (HAc)	100mM HAc	CON??	0.1mM	1h		[213]
Creatinine, GABA,BALA			10mM HCl	3.3 (BALA)	100mM HAc	CON??	0.1mM	1h		[213]

Organic acids	PO_4^{3-}, SO_4^{2-}		10mM HCl, 0.05% Mowiol, 0.2% HEC	2.9 (BALA)	5mM propionic acid (pH 7 by NaOH)	CON, UV (254nm)	Over 0.1mM	250s		[70,97]
Organic acids			10mM HCl	6.0 (His)	10mM aspartic acid	CON, UV	10mM	400s		[214]
Organic acids, codeine	PO_4^{3-}		10mM HCl, 0.2% HEC	6.0 (His)	5mM MES	CON, UV (254nm)	0-4nM	900s		[177]
Organic acids, codeine	PO_4^{3-}		10mM KOH, 0.05% Mowiol	5.0 (HAc)	5mM HCl	CON, UV (254nm)	0-4nM	900s		[177]
Organic acids, codeine	PO_4^{3-}		10mM KOH, 0.05% Mowiol	5.0 (HIBA), 4.2 (HAc)	5mM HCl	CON, UV (254nm)	0-4nM	900s		[177]
Organic acids	PO_4^{3-},PO_3^{3-}, ClO_3^-, Br^-		6.6mM HCl	4.2 (aniline)	1.2mM HAc	NON CON, UV	0.8-2mM	300s		[178]
Organic acids	PO_4^{3-}, SO_4^{2-}		10mM HCl, 0.2% HEC	6.0 (His)	5mM MES	CON	??	600s		[179]
Organic acids	PO_4^{3-}		10mM HCl	6.0 (His)	10mM caproic acid	CON, UV (254nm)	??	??		[183]
Organic acids			PRE-SEPARATION:10mM HCl-His, 0.2% MHPC ANALYTICAL: 6mM HCl-His, 6mM His, 2mM $CaCl_2$, 0.1% HEC	6.0 (His)	10mM CITR	CON, UV (254nm)	??	??		[183]
Organic acids			6mM HCl-His, 6mM His, 2mM $CaCl_2$, 0.1% HEC	6.0 (His)	10mM CITR	CON, UV (254nm)	??	1700s		[183]
Amaranth, methyl orange, bromophenol blue			10mM HCl, 0.1% HEC	6.0 (His)	10mM MES (H 6.0 by His)	CON	0.5-1mM	150s		[68,123]
Organic acids			10mM HCl, 22mM EACA, 0.05% HPMC, 15% isopropanol		5mM caproic acid	CON	0.1mM	1200s		[135]
Organic acids	CO_3^{2-}		10mM HCl	7.2 (imidazole)	5mM disodium tetraborate	CON CON	0.025-0.5mM	1100s		[95]
Organic acids	PO_4^{3-}		10mM HCl, 0.1% HEC	5.5 (His)	10mM hexanoic acid	CON CON	0.025-0.5mM	1100s		[95]
caproate	Cl^-,F^-, Br^-		10mM KI (sol: CH_3OH)		10mM palmitic acid (sol: CH_3OH)	POT, CON	??	1500s		[107]

BF^-			8mM HCl, 3mM BTP, 0.1% HEC	3.55 (BALA)	2mM CITR	CON CON	0.1-0.4mM	1400s		[215]
Organic acids			10mM HCl	6.0 (His)	Glutamic acid	THE	5-10mM	??		[215]
Organic acids			10mM H_2SO_4	4.2 (BALA)	0.6mM phenylacetic acid	CON, UV	0.05-6mM	200s		[216]
Organic acids			10mM HCl, 15-30mM BALA	3.1-3.7	10mM propionic acid	POT, UV (254nm)	??	??		[217]
Organic acids			10mM HCl, 15-30mM EACA	4-4.7	10mM propionic acid	POT, UV (254nm)	??	??		[217]
Organic acids			10mM HCl, 15-30mM pyridine	4.7-5.4	10mM propionic acid	POT, UV (254nm)	??	??		[217]
Organic acids			10mM HCl, 15-30mM His	5.6-6.3	10mM propionic acid	POT, UV (254nm)	??	??		[217]
Organic acids			10mM HCl, 20mM imidazole	6.95	10mM propionic acid	POT, UV (254nm)	??	??		[217]
Organic acids			10mM HCl, 20mM Tris	7.8	10mM propionic acid	POT, UV (254nm)	??	??		[217]
Organic acids			10mM HCl	3.0 (BALA)	Caproic acid	??	??	??		[218]
Organic acids			10mM HCl	5.0 (creatinine)	Caproic acid	??	??	??		[218]
Organic acids			10mM HCl	7.0 (imidazole)	MOPS	??	??	??		[218]
Organic acids			10mM HCl	9.0 (ammediol)	Glycine	??	??	??		[218]
Amaranth			10mM HCl, 0.05% HEC	6.0 (His)	10mM MES (pH 6.0 by His)	POT	0.05-1mM	??		[219]
Phytic acid			10mM HCl, 2mM BTP	4.5 (EACA)	5mM caproic acid	NON CON	0.01-0.12mM	200s		[130,220]
Phytic acid			10mM HCl	5.0 (His)	5mM caproic acid	NON CON	0.01-0.12mM	200s		[130,220]
Phytic acid			10mM HCl	6.1 (BTP)	5mM MES	NON CON	0.01-0.12mM	200s		[130,220]
Organic acids			10mM HCl, 0.1% MHEC	3.5 (BALA)	5mnM caproic acid, 5mM His	CON	??	??		[93]
Organic acids			5mM HCl, 0.1% MHEC	3.5 (BALA)	5mM caproic acid	CON	0.5-10mg/l	??		[93,221]
Organic acids	SO_4^{2-}, PO_4^{3-}		10mM HCl, 0.2% Mowiol	6.0 (BTP)	5mM caprylic acid (pH 8.0 by Tris)	CON	??	??		[70]
Organic acids	PO_4^{3-}		5mM HCl	2.8 (Gly)	5mM caproic acid	CON	??	??		[70]
Organic acids			10mM HCl, 0.1% MHEC	3.2 or 3.5 (BALA)	5mM caproic acid (pH 6.0 by His)	CON	100μM-1mM	??		[68]

Glutamate, benzoate, parabens, sorbate			10mM HCl, 0.2% MHEC	6.15 (His)	8mM MES (pH 6.2 by His)	CON	60-450μM	500s		[68,196]
Glutamate, benzoate, parabens, sorbate			10mM HCl, 0.2% MHEC	9.5 (BTP)	10mM BALA (pH 10. By BTP)	CON	60-450μM	800s		[68,196]
Glutamate, benzoate, parabens, sorbate			10mM HCl, 0.2% MHEC	3.9 (BALA)	10mM propionic acid (pH 4.7 by EACA)	CON	60-450μM	300s		[68,196]
Glutamate, benzoate, parabens, sorbate			10mM HCl, 0.2% MHEC	5.7 (His)	8mM MES (pH 6.0 by His)	CON	60-450μM	250s		[68,196]
Organic acids			10mM HCl, 3mM $MgCl_2$, 0.01% Mowiol	8.5 (Tris)	10mM BALA (pH 10.4 by KOH)	POT	0.5-21nM	2000s		[72,222]
fumaric acid	SO_4^{2-}, PO_4^{3-}		10mM HCl, 0.05% HPMC	3.0 (BALA)	10mM CITR	CON, UV (254nm)	25-1000ng/ml	500s		[185]
fumaric acid, tartaric acid	SO_4^{2-}, PO_4^{3-}		10mM HCl, 5mM β-CD, 0.05% HPMC	3.0 (BALA)	10mM CITR	CON, UV (254nm)	25-1000ng/ml	500s		[185]
fumaric acid, tartaric acid		(fumaric acid, tartaric acid)	10mM HCl, 0.05% HPMC	3.0 (BALA)	10mM CITR	CON, UV (254nm)	25-1000ng/ml	450s		[185]
Orotic acid	PO_4^{3-}		100mM HCl, 14.5mM BALA, 0.2% HEC	3.25	5mM Asp	CON, PHO (218nm, 280nm)	5nM	200s??		[27]
Orotic acid	PO_4^{3-}		100mM HCl, 14.5mM BALA, 30mM α-CD, 0.2% HEC	3.25	5mM Asp	CON, PHO (218nm, 280nm)	5nM	200s??		[27]
Benzoic acid isomers			10mM HCl, 0.1% PVA, 0-16mM α- or β- or γ-CD	5.1 (creatinine)	10mM MES (pH 6.0 by Tris)	CON	??	300s??		[223]

Benzoic acid isomers			10mM HCl, 0.1% PVA, 0-16mM α- or β- or γ-CD (sol: 10-30% CH_3OH)	5.1 (creatinine)	10mM MES (pH 6.0 by Tris)	CON	??	300s??		[223]
Benzoic acid isomers			10mM HCl, 0.1% PVA, 0-16mM α- or β- or γ-CD (sol: 20% C_2H_5OH)	5.1 (creatinine)	10mM MES (pH 6.0 by Tris)	CON	??	300s??		[223]
Astrazon pink, toluidine blue			1mM KOH, 19mM NH_4OH, 10mM HIBA, 0.2% HEC	4.8 (HAc)	10mM Car Hydro	POT, PHO	150nM, 5mM	1800s		[155]
Imidazolium cations			10mM NH_4OH, 0.1% HEC	5.0 (CH_3COOH)	5mM TBA	CON CON	0.1-0.2mM	1700s		[215]
Urea			10mM TMA, 168mM HAc, 0.2g/l HPMC (sol: 95% CH_3OH)	5.6	20mM NaOH, 140mM HAc (pH 5.8), (sol: 95% CH_3OH)	POT, UV (254nm)	0.5-64mM	1350		[224]
Herbicides (CCC)			10mM KOH, 0.05% PVA	4.7-5.4 (by HAc)	5mM Tris (pH 5.0 by HAc)	CON	5-10mM	1000s??		[225]
Herbicides (diquat)			10mM KOH, 0.05% PVA	6.0 (CITR)	5mM Tris (pH 5.8 by HAc)	CON	5-10mM	1000s??		[225]
Herbicides (paraquat)			10mM KOH, 0.05% PVA	7.4 (diiodotyrosine)	5mM Tris (pH 7.0 by HAc)	CON	5-10mM	1000s??		[225]
Herbicides (s-triazines)			10mM KOH, 0.05% PVA	5.0 (HAc)	20mM Gly	CON	5-10mM	1000s??		[225]
Humic substances			10mM HCl, 0.1% HEC, 0-2.5% PVP	3.5 (BALA)	5mM caproic acid	PHO (405nm)	0.05mM	500s??		[226]
Protein samples			20mM triethylamine	4.4 (HAc)	10mM HAc	SPH, UV (214nm)	0.2-2nM	900s		[227]
Urine samples			40mM HCl, 0.2% MHEC	6.0 (His)	10mM MES (pH 6.0 by His)	UV (254nm)	??	500s		[228]
Urine samples			25mM HCl, 0.2% MHEC	3.3 (BALA)	10mM propionic acid (pH 4.0 by BALA)	UV (254nm)	??	500s		[228]

Asp,Glu,Gly	(His,Phe); (Ala,Val)		10mM HCl	9.0 (ammediol)	10mM BALA (pH 9.0 by B a$(OH)_2$)	CON	??	1200s		[229]
Asp,Glu,Gly	(His,Phe); (Ala,Val)		10mM HCl	9.0 (Den)	10mM BALA (pH 9.0 by Ba$(OH)_2$)	CON	??	1200s		[229]
Glu,Asp,BALA, Val,Phe,Ala,Gl y			5mM $CuCl_2$, 5mM Den	9.0 (NaOH)	10mM His (pH 9.0 by Ba$(OH)_2$)	CON	??	1200s		[229]
Glu,BALA	(Phe,Val,Ala); (Asp,Gly)		5mM $CuCl_2$	9.0 (Den)	10mM His (pH 9.0 by Ba$(OH)_2$)	CON	??	1200s		[229]
Glu,Asp,Phe	(Gly,Ala); (Val,BALA)		3mM $CuCl_2$, 4mM HCl	9.0 (Den)	10mM His (pH 9.0 by Ba$(OH)_2$)	CON	??	1200s		[229]
Glu	(Asp,Glu); (His,Phe); (Ala,Val)		1mM $CuCl_2$, 8mM HCl	9.0 (Den)	10mM BALA (pH 9.0 by Ba$(OH)_2$)	CON	??	1200s		[229]
Doxorubicin, carminomicin, epirubicin			10mM His, (sol: 60% CH_3OH)	7.2	10mM Na_3PO_4 (sol: 60% CH_3OH)	CE-MS	5mg/ml	1500s		[230]
Tryptophan			10mM HCl, 0.2% MHEC	9.3 (BTP)	10mM borate (pH 9.0 by BTP)	CE, PHO, CON	0.5-0.8μmol/l	3000s		[231]
Ibuprofen, diclofenac			10mM formic acid	2.9	10mM propionic acid	MS	0.25-2.5nM	750s		[93,232]
Amines			5mM Ba$(OH)_2$, 1% HEC	8.5 (15mM Val)	20mM Tris (pH 8.3 by 10mM HCl)	CON	10-100mg/l	600s		[93,233]
Chondroitin sulphate			5mM HCl, 10mM Gly, 0.01% HEC	2.8	10mM CITR	CON CON, UV (254nm)	1-50mg/ml	1000s		[93,234]
Troponin			20mM KOH, 0.5M urea, 1% Triton X-100, 2% PVP	8.0 (HEPES)	60mM His, 0.5M urea, 1% Triton X-1002% PVP (pH 7.2 by HEPES)	??	8-40μg/ml	600s	150mM NaCl added to sample	[93,234]

N-acetylcysteine			10mM HCl, 20mM His, 0.1% MHEC	6.0	10mM MES, 12mM His, 0.1% MHEC	CON	25-200mg/l	400s		[93,235]
Bacteria cells			50mM HCl, 0.5% PVP	8.0 (His)	0.5-5mM Tris (pH 7.8 by HEPES)	CON	0-4*10^4 cells/ml	900s		[93,236]
Cardiovascular drugs			10mM NaOH, 0.1% MHEC	5.5 (MES)	5mM Glu	CON	100-2500ng/ml	1500s		[93,237]
Cardiovascular drugs			10mM HCl, 0.1% MHEC	6.2 (His)	5mM MES	CON	100-2500ng/ml	1500s		[93,237]
β-blockers			10mM NaOH, 0.1% MHEC	5.5 (MES)	30mM H_3PO_4	CON	25μg/ml	500s		[68,238]
β-blockers			10mM NaOH, 0.1% MHEC	5.5 (MES)	5mM glutamic acid	CON	25μg/ml	500s		[68,238]
Synthetic colourants in food			10mM BALA, 0.1% MHEC	3.5	5mM HAc	CON	100mg/l	1800-2400s		[239]
Synthetic colourants in food			10mM EACA, 0.1% MHEC	4.5	5mM CAPR	CON	100mg/l	1800-2400s		[239]
Synthetic colourants in food			10mM His, 0.1% MHEC	6.0	5mM CAPR	CON	100mg/l	1800-2400s		[239]
Synthetic colourants in food			10mM His, 0.1% MHEC	6.0	5mM His	CON	100mg/l	1800-2400s		[239]
Phenolic compounds			10mM HCl, 0.2% HEC (sol: 20% CH_3OH)	7.2 (Tris)	50mM H_3BO_3 (pH 82 by $Ba(OH)_2$) (sol: 20% CH_3OH)	CON	0.125-2.5μg/ml	800s		[240]
Clenbuterol			10mM NH_4Ac	2.5 (HAc)	10mM BALA (pH 2.5 by HAc)	UV (214nm)	10ppb	1600s	Made in 1mM HAc	[241]
nophenol, diaminobenzene isomers			10mM KOH, 0.4% PVA, 0-20mM α- or β-CD	5.4 (picolinic acid)	5mM HAc	CON	1-1.5ppb	1200s		[242]

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