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Determination of copper species in atmospheric waters

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Abstract

The total copper concentration was determined in rainwater and roof runoff collected in Plymouth, UK between Sept-Oct 2013. The concentration was measured using inductively coupled plasma mass spectrometry and found to be 2.19 ± 0.456 and $3.18 \pm 0.506 \mu\text{g L}^{-1}$ for rainwater and roof runoff, respectively. These were found to coincide with other published rainwater Cu concentrations. The method itself showed poor accuracy, with a 77.6% recovery for Cu.

A method for the determination of Cu(I) by ultraviolet-visible spectrophotometry using bathocuproine was also evaluated. A series of Cu(I)Br calibration standards between concentrations of 0.05 and 0.5 mM were used to assess the absorbance of the $[\text{Cu}(\text{BCP})_2]^+$ complex at a various pH ranges. Ethylenediamine was used to mask interferences caused by Cu(II). The $[\text{Cu}(\text{BCP})_2]^+$ complex was observed to be most stable as a pH >8.0, resulting in the highest absorbance throughout the pH ranges. Opened and closed systems were used to evaluate the oxidation of Cu(I) in the presence of air. The open system saw a small decrease in absorbance, inferring the oxidation rate of Cu(I) was not rapid, with only a partial Cu(I) oxidation. The limit of detection for Cu(I) using this method was found to be 1.11×10^{-4} M, concluding that the method was unsuitable for quantifying Cu(I) in atmospheric waters.

Introduction

Sources of copper

Copper is the 26th element in order of abundance on Earth, comprising around 50 ppm (0.007%) of the Earth's crust, 20 ppm of soils, and 0.2 ppb of sea water (Emsley, 2001). Many factors contribute to the concentration of Cu found in atmospheric waters. Large quantities of anthropogenic and natural material are emitted into the atmosphere daily (Başak & Alagha, 2004). Natural sources such as windblown dust, volcanoes, vegetation exudates, sea-salt sprays and forest fires (Gaetke & Chow, 2003) contribute to approximately 18.5×10^6 kg of Cu into the atmosphere annually (Kieber *et al.*, 2004).

Anthropogenic activities however are now the principle source of many trace elements found in the atmosphere. Activities include combustion of fossil fuels, roasting of ores for refining metals, processing of crustal materials for manufacturing cements, and burning of waste materials, (Allen, 1993). Automobile traffic was also identified as a major contributor, responsible for ~65% of the total Cu emissions in the United Kingdom. A result of such activities is approximately 56×10^6 kg of Cu entering the atmosphere annually; a total of more than 74.5×10^6 kg of Cu annually entering by both anthropogenic and natural sources, which are removed by rainfall. See Adriano (2001) for a list of the various natural and anthropogenic sources of copper, as well as the common forms of copper found in the environment as a result.

Chemistry of copper

Copper belongs to group 11 of the periodic table. Like other members of the group (silver and gold), copper as an element is a relatively inert, corrosion-resistant metal with high malleability and conductivity (Ropp, 2013). The element has an atomic number of 29, and an atomic mass of 63.546(3) u. It has two common oxidation states of (I) and (II); however oxidation states of (III) and (IV) are possible, in fluorides such as K_3CuF_6 and Cs_2CuF_6 , respectively (Wiberg, Holleman & Wilberg, 2001). The cuprous ion (Cu^+) is far less stable than the cupric ion (Cu^{2+}), and is readily oxidised. There are two common naturally occurring stable isotopes, ^{63}Cu and ^{65}Cu , with natural abundances (atom %) of 69.17 and 30.83, respectively. There are also nine naturally occurring radioisotopes of copper, with masses ranging from 59 to 69. Copper has the ground state electron configuration of $[Ar] 3d^{10} 4s^1$, and is the second heaviest of the first row transition metals.

Like the other metals in the period table, copper can form coordination complexes with ligands. In aqueous solution, copper (II) primarily exists as the hexaaquacopper(II) ion, $[Cu(H_2O)_6]^{2+}$. This complex exhibits the fastest water exchange rate (speed of water ligands attaching and detaching) of all the transition metal aquo complexes. This complex can also go on to form numerous complexes if other ions are present in solution. For example the neutral complex $[Cu(H_2O)_4(OH)_2]$ can form if hydroxide ions are present, as well as with ammonia when acting as a base. Ammonia can also act as a ligand itself, replacing water as a ligand and forming $[Cu(NH_3)_4(H_2O)_2]^{2+}$ (Cotton & Wilkinson, 1998).

The pH of the aqueous medium can also greatly influence the chemistry and speciation of the Cu. For example, saline waters are affected largely by pH; with

decreasing pH (increasing H^+ activity) Cu^{2+} and $CuSO_4$ are more present at the expense of $CuCO_3$. The extraction of copper by lipid layers is also affected by pH (Blust *et al.*, 1987).

The variation in hydrated species and solid copper compounds not only depend on the pH-value, but also on the oxidation states of copper, i.e. on redox potentials.

Importance of copper speciation in the environment

The speciation of a metal is important for the determination of its reactivity and bioavailability in natural waters (Wang & Chakrabarti, 2008). Transition metals are common constituents of cloud droplets, raindrops and other atmospheric droplets (Graedel, Weschler & Mandich, 1985). Copper is one of the most abundant transition metals present (Allen, 1993), found both in dissolved and particulate forms (Witt & Jickells, 2005), with a volume-weighted average total copper concentration of 5.3 ± 0.9 nM, with 76% dissolved (Kieber *et al.*, 2004). The majority of early research done on total or dissolved copper in atmospheric waters does not measure or account for the speciation (Allen, 1993).

Copper exists in two oxidation states in natural waters; Cu(I) and Cu(II). Speciation is particularly important as copper is involved in many important redox reactions in the atmosphere, such the oxidation of SO_2 , and the cycling of OH, H_2O_2 and O_2^- (Xue & Sigg, 1993). The speciation of other trace metals in the troposphere including iron and chromium is also affected by Cu speciation (Zuo, 1995). The oxidation state and chemical form of metals is also known to greatly influence their bioavailability as reflected by their toxicity (Allen, 1993). Much of the concerns over the effect of copper on the environment relate to measurements of total dissolved copper, however organically bound copper is considered to be largely non-toxic (Jones & Bolam, 2007), illustrating the importance of identifying the speciation of the metal.

An uncertainty with great importance with regard to Cu speciation is the degree to which it is organically complexed. This directly impacts the chemistry of atmospheric waters since the free hydrated Cu ion controls the catalytic capabilities for reactions such as SO_2 oxidation (Weschler, Mandich & Graedel, 1986). Earlier studies have also suggested that organic complexation is responsible for the relatively high abundance (25%) and unusual stability of Cu(I) in rainwater (Kieber *et al.*, 2004). Dissolved organic carbon (DOC) is well known to form complexes with heavy metals, playing an important role in controlling heavy metal speciation (Christensen, Botma & Christensen, 1999). The area of Plymouth is known to have a high level of dissolved organic matter in marinas and rivers, likely due to run off from moorlands (Jones & Bolam, 2007).

Environmental impact of copper concentrations and toxicity

Copper is an essential trace nutrient to all species (Durukan, Arpa Şahin & Bektaş, 2011), having a range of uses such as copper-dependent enzymes; examples are c oxidase for cell energy production, and superoxide dismutase for protection against free radicals (Emsley, 2001). An adult human needs to ingest around 1.2 milligrams of copper a day. However it can become harmful are high concentrations (Sahin, Tokgöz & Bektaş, 2010). It is well established that copper exerts toxic effects on aquatic species such as bacteria, plants and fish, with copper being a major ingredient in many algaecides and herbicides (Nason, Sprick & Bloomquist, 2012).

The estimated lethal dose of Cu in an untreated adult is about 10-20 g. Acute and chronic Cu toxicity in humans is relatively rare (Gaetke & Chow, 2003), as most humans and animals are able to control excess amounts of Cu in the body by either decreased absorption or increased excretion. However, prolonged exposure to Cu may result in weakness, lethargy, vomiting, and conditions relating to necrosis of the liver and kidney. Copper has also been linked to the pathogenesis of neurodegenerative disorders, such as Alzheimer's disease, Parkinson's disease, and amyotrophic lateral sclerosis (Pal, 2014).

The major concern of Cu concentration in atmospheric waters is its effect on marine and plant life. Nason et al. (2012) illustrated $<2 \text{ mg L}^{-1}$ Cu was capable of inhibiting the olfactory senses of juvenile Coho salmon, with Smith (1993) reporting growth reduction in the amphipod *Allorchestes compressa* following 4 weeks exposure of $9\text{-}10 \mu\text{g L}^{-1}$ of Cu. Pérez, Beiras & Fernández (2010) reported the effective concentration to observed a 10% reduction in Phytoplankton as $2.65 \mu\text{g L}^{-1}$. Allen (1993) also discusses how high concentrations of copper can damage the cell membranes and walls of many plants.

The free Cu^+ and Cu^{2+} ions are the most toxic forms to marine life, with toxicity decreasing in the order, Cu^+ and $\text{Cu}^{2+} >$ inorganic copper $>$ organic copper. However upon entering natural waters free copper is quickly complexed to carbonates, hydroxides and bound by organic ligands, reducing its effect on the marine species (Jones & Bolam, 2007).

Sampling and sample preparation of rainwater

The majority of research undertaken on the analysis of trace metals and ligands in atmospheric waters follows similar techniques and protocols when sampling. Due to the low level of analytes in the samples, considerable precautions are needed in ensuring no contamination occurs. Duinker and Kramer (1977) stated that most errors are introduced during sampling, filtration and storing the samples due to introduction of metals from dust or the equipment used.

The collection of samples usually involves relatively cheap and simple storage vessels; polyethylene bottles or fluorinated-high density polyethylene (FLPE) bottles were used for sampling in Jin & Gogan (2000) with many others using 'home-made' apparatus, consisting of a high density polyethylene (HDPE) funnel mounted inside a polypropylene bucket containing a 5 L HDPE bottle to collect rain samples (Başak & Alagha, 2004). Plavšić et al. (2008) also incorporated brown glass bottles for collection of samples, likely due to some species being oxidised by sunlight. Each of these methods involved using acid washed containers. Jones and Bolam (2007) also stored sample bottles in polythene bags to reduce the risk of contamination. Analysis was carried out as swiftly as possible, typically the following day, due to possible composition changes in the sample (Kieber *et al.*, 2004).

Analytical method for determination of copper

Several analytical techniques have been published for the determination of trace metals in atmospheric waters. Spectroscopic techniques are among the most common used; these include atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled

plasma mass spectrometry (ICP-MS). However, the determination of trace metal ions in natural waters can be difficult due to various factors, particularly their low concentrations and matrix effects (Ghaedi *et al.*, 2008).

Conventional flame atomic absorption spectrometry (FAAS) is less frequently used for measurements; it is often required to perform a pre-concentration for samples due to its limited sensitivity (a result of poor efficiency of the nebulizer/burner system) (Matusiewicz, 1997). Many ions such as K^+ , Na^+ and Zn^{2+} have been shown to cause a potential interference in natural water samples on determination of the analyte when using FAAS (Durukan *et al.*, 2011). Viable pre-concentration techniques commonly used include Cloud Point Extraction (Chen & Teo, 2001; Manzoori & Bavili-Tabrizi, 2002) and Atom Trapping (Matusiewicz, 1997), which have shown to be a possible alternative to graphite furnace atomic absorption spectrometry GF-AAS (Hallam & Thompson, 1985), increasing sensitivity up to 270 times. However these techniques require additional time and effort; they can greatly increase the necessary sample volume, as well as introducing further possible errors.

Graphite furnace atomic absorption spectrophotometry (GF-AAS) is among the most commonly used technique for atmospheric trace metals measurements (Christensen, Botma & Christensen, 1999; Kieber, Williams & Willey, 2001; Witt & Jickells, 2005), largely due to the low levels of detection needed. Ratttonetti (1974) recommended GF-AAS due to its small sample volume (20 μ L) requirements and low absolute detection capability, measuring samples in the $ng\ ml^{-1}$ range and below.

In recent years atmospheric water analysis is becoming more commonly performed by ICP-MS (Montoya-Mayor *et al.*, 2013; Moreda-Piñeiro *et al.*, 2014) due to high sensitivity and speed of analysis. EPA Method 200.8 for the determination of trace elements in waters and wastes (US EPA, 1994) also recommends the use of ICP-MS for analysis.

Determination of copper speciation in water samples is commonly analysed using variation of anodic/cathodic stripping voltammetry (ASV/CSV) techniques, often coupled with a competitive ligand exchange (Oldham, Swenson & Buck, 2014; Wang & Chakrabarti, 2008; Cheng *et al.*, 1994). ASV works by reducing the analyte species upon a working electrode. An oxidising potential sweep is then applied to the electrode and the analyte is re-oxidised at its characteristic oxidation potential; the cathodic current generated is proportional to the amount of analyte initially deposited onto the electrode (Wang, 1983). The popularity of the technique is a result of its high sensitivity (low ppb-high ppt) and reproducibility (RSD <5%), with little expense (Bard & Faulkner, 2001).

An alternative to these highly sensitive techniques is the determination of Cu speciation using bathocuproine via UV-Visible spectrophotometry. Moffett and Zika (1983) outlines a method for determining Cu(I) concentrations in natural waters using this technique. By using the bathocuproine ligand to complex a series of Cu(I)Br standards, each absorbance can be measured and used for quantifying Cu(I) in a sample of unknown concentration. This method has been shown to be viable for many different samples (Lu *et al.*, 2003), however due to its lower sensitivity

compared to ASV (10^{-6} M compared to 10^{-9} M), it is likely unsuitable for atmospheric waters. A variation of this spectrophotometric technique commonly used is using neocuproine in place of bathocuproine. This was shown to have similar results as using bathocuproine, with detection limits for Cu(I) of 1×10^{-6} – 1×10^{-4} mol L⁻¹ (Tutem, Apak & Baykut, 1991). The method using bathocuproine was evaluated to see whether it is a suitable alternative to when stripping voltammetry techniques are not available for the determination of Cu(I) concentration.

Due to its many advantages, inductively coupled plasma mass spectrometry was selected for the determination of total copper concentrations in rainwater and roof runoff samples. A rapid, simple and relatively simple analytical method, it is capable of the lowest detection limits, eliminating the need for pre-concentration of samples.

Principles of ICP-MS

As the name suggests, inductively coupled plasma mass spectrometry consists of two main parts; a plasma ion source and a mass spectrometry detector. Plasma is an ionized gas that is macroscopically neutral, having an equal concentration of positive particles (ions) to negative (electrons), making the gas electrically conductive. Argon gas is used in ICP-MS, and is partially ionized using an electromagnetic coil ($\text{Ar} \rightarrow \text{Ar}^+ + \text{e}^-$). Samples are introduced into the Ar plasma as aerosol droplets, via a nebulizer and spray chamber. Upon meeting the plasma they are dried and all molecules present dissociate (atomization). Each component then has an electron removed, forming singly-charged ions ($\text{M} \rightarrow \text{M}^+ + \text{e}^-$) (Dass, 2006). This ionization step is very efficient, approaching 100% of all atoms for some elements (e.g. sodium), but this is dependent on the ionization potential (PerkinElmer, 2011).

Next a fraction of ions formed are drawn through two cones of varying size, sampler and skimmer (commonly made of Ni or Pt), allowing a vacuum to be formed which is required for the mass spectrometer. The vacuum is made by a series of peristaltic pumps, providing the correct operating pressures. The initial rotary pump creates a pressure ranging 10^0 - 10^{-1} Torr between the two cones, whereas turbomolecular pumps create pressures ranging 10^{-4} - 10^{-5} Torr for the mass spectrometer. Before the ions can enter the mass spectrometer for analysis possible sources of interference present must be removed. The beam of ions contains neutral molecules and atoms, which can create drift by collecting on instrument components, and photons, which can increase background by being counted for ions. Before the quadrupole, a reaction/collision cell (also known as universal cell) is often present to eliminate interferences caused by polyatomic species that form between the Ar and sample matrix that have the same m/z of the analyte. Reaction cells consist of a chamber filled with reaction gases that react with the introduced sample, suppressing plasma-based isobaric interferences (Tanner & Baranov, 1999). Collision cells however introduce a collision gas (He), or reactive gas (H₂), which induces additional collisions and reactions which dissociate polyatomic species, eliminating interferences.

The mass spectrometer commonly consists of two parts; one or more quadrupoles and the detector. The quadrupole mass filter consists of four parallel electrically conducting rods; opposing rods are connected and parallel rods are supplied with a

DC voltage, a pair held at a positive voltage, a pair at negative (De Hoffmann & Stroobant, 2007). The applied voltages affect the trajectory of ions traveling down the path centred between the rods. Only ions of a certain mass-to-charge ratio (m/z) pass through the quadrupole filter and all other ions are thrown out of their original path.

Having separated ions in terms of their m/z , the ions then exit the quadrupole and hit the active surface of the detector, commonly a continuous dynode, which will release an electron for each ion impacting. Each electron released strikes additional dynodes amplifying the signal, which in turn release more, continuing until a measurable pulse of raw counts is produced which can be quantified by the data handling software (Hill, 1999).

In a typical quantitative analysis, the concentration of each element is determined by comparing the counts measured by the detector for a selected isotope to an external calibration curve that was created for that element. This external calibration method consists of preparing a series of standards with known concentrations of the analyte of interest (M_{ste}), then recording the intensity of the response signal (I_{ste}) for each standard. Then without any modifications to the analytical conditions, the sample containing the analyte to be quantified (M_x) can be measured for its intensity of response signal (I_x). As long as the response signal intensity is linear in regards to concentration of analyte, the concentration of the analyte in the sample can be calculated using Equation 1 (De Hoffmann & Stroobant, 2007).

$$M_x = I_x \times \frac{M_{ste}}{I_{ste}} \quad \text{Equation 1}$$

The instrument detection limit of ICP-MS for copper can be as low as $0.1\text{-}1 \text{ ng L}^{-1}$. However EPA method 200.8 (US EPA, 1994) stated the method detection limit for copper in an aqueous solution was $0.5 \text{ } \mu\text{g L}^{-1}$. There are also possible polyatomic interferences to consider when analysing for Cu. For example, polyatomic overlays originating from Na^+ and Mg^{2+} matrix elements due to the formation of $^{40}\text{Ar}^{23}\text{Na}^+$ and $^{40}\text{Ar}^{25}\text{Mg}^+$ in the m/z ratios of 63 and 65, respectively. Chrastný and Komárek (2009) discussed the use of He/ H_2 collision cells to eliminate these interferences. The ICP-MS instrument in this experiment had a collision cell with 7% H in He introduced at flow rate of 3.5 mL min^{-1} to reduce these polyatomic interferences.

Principles of UV-Vis spectrophotometry

Ultraviolet-Visible (UV-Vis) spectrophotometry relates to the absorption spectroscopy within the ultraviolet-spectral region of the electromagnetic spectrum, utilizing light in the visible (400-780 nm) and near-UV (200-400 nm). It is commonly used in analytical chemistry for a quantitative determination of an analyte (Thomas, 1996).

The electrons in a molecule when imparted with energy from light radiation can become excited, moving to a higher molecular orbital. π bond and non-bonding electrons are readily excited by near-UV and visible light (Skoog *et al.*, 2003). By using a spectrophotometer, the degree of absorption by a sample at different wavelengths can be measured. The absorbance can then be plotted against the wavelength to produce a spectrum. The absorbance can also be used to calculate

the concentration of the absorbing species by using the Beer -Lambert Law, shown in Equation 2 (Harris, 2010).

$$A = \varepsilon \cdot c \cdot l \quad \text{Equation 2}$$

Where ε is the molar absorptivity ($\text{L mol}^{-1} \text{cm}^{-1}$), c is the concentration (mol L^{-1}) and l is the path length (cm).

By preparing a series of standards with known concentrations of the analyte of interest, the absorbance for each standard can be measured, allowing a calibration curve to be plotted from which the concentration of an unknown can be calculated from its measured absorbance.

There are three key components to a diode array spectrophotometer (as used in this experiment); the source, the polychromator, and the diode array. The source is where the light is emitted in order to excite the sample under analysis. This usually consists of a deuterium lamp for UV radiation (emitting 180 nm to 370 nm), and a tungsten lamp for visible light (emitting 350 nm to 900 nm) (Skoog *et al.*, 2003). The radiation emitted is narrowed and directed via a lens, where it then passes through the sample chamber where the sample is contained in a quartz cuvette. Quartz must be used as glass absorbs all wavelengths <300 nm. The light then exits the sample where it is refocused with a lens through a slit used to reduce ambient light interferences (Laqua *et al.*, 1995). The light then hits a polychromator (grating), where it is spatially split up into individual wavelengths. The dispersed light then hits the photodiode array detector, commonly consisting of 1024 photodiodes, where the light intensity is converted to an electrical signal for each wavelength. This allows for the absorbance of light at each wavelength by the sample to be quantified (Ryan, Miller & Ingle, 1978).

The determination of copper species using UV-Vis spectrophotometry has been used in many different samples ranging from seawater, jet fuels and food samples) (Lu *et al.*, 2003; Moffett & Zika, 1983). Various different complexation ligands other than bathocuproine (BCP) have also been successfully used, such neocuproine, 1,5-bis(di-2-pyridylmethylene) thiocarbonohydrazide (DPTH), and glyoxal bis(4-phenyl-3-thiosemicarbazone) (GBPT) (Tutem, Apak & Baykut, 1991; Jiménez, Herrador & Asuero, 1989). For the determination of Cu(I) using bathocuproine, a detection limit of 1×10^{-6} M was achieved for a seawater sample (Moffett & Zika, 1983). The characteristic absorbance for the Cu(I) bathocuproine complex was 480 nm. Figure 1 shows the $[\text{Cu}(\text{BCP})_2]^+$ complex.

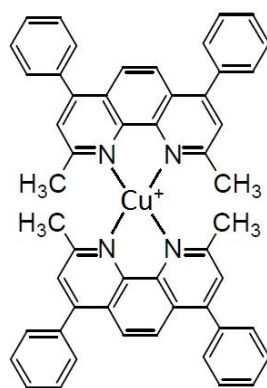


Figure 1: Structure of the $[\text{Cu}(\text{BCP})_2]^+$ complex

Aims and objectives

It has been shown that little is known about the speciation of Cu found in rain water samples. However it is well established speciation has an effect on the toxicity to marine life, with rainwater Cu having a large deposition into marine waters. Cu speciation is also documented in playing an important role in the speciation of other trace metal in rainwater and sea water (Zuo, 1995).

This project aims to quantify Cu concentrations in both Plymouth rainwater and residential roof runoff water (as a comparison to rain water) using ICP-MS, and briefly assess possible causes for differences in concentrations. It also aims to develop and optimise a spectrophotometric method for redox speciation of Cu(I) in synthetic samples using bathocuproine, evaluating the overall performance of the method and whether it would be suitable for atmospheric water samples.

Experimental

Apparatus

All laboratory ware (glass and plastics) used in contact with samples and reagents were cleaned prior to use, using the procedure that follows. The laboratory ware was rinsed with deionised water before being placed to soak in a weak (0.1%-1% v/v) detergent bath (i.e. Decon 90) overnight. The laboratory ware was then removed and rinsed again with deionised water three times to remove the bubbles and soap residue, before being placed to soak in a 10% v/v hydrochloric acid (HCl) bath overnight. It was then removed and rinsed three times with deionised water and once with Milli-Q water (Millipore 18.2 MΩ cm) before use.

For the 25 L polypropylene (PP) containers the following modified cleaning procedure was used due to the container sizes. The containers and lids were rinsed 3 times with deionized water then once rinsed over with a weak (0.1-1% v/v) detergent bath (i.e. Decon 90). The containers were then once again rinsed 3 times with deionized water to remove soap/bubbles. Containers were then rinsed thoroughly with ~4M HCl, followed by extensive rinsing with Milli-Q water three times. Containers were then closed and stored in large black refuse sacks until sample collection. Volumetric flasks used for the calibration standards for ICP-MS analysis

were rinsed and filled with 2% Nitric Acid before being left to soak overnight prior to use.

Reagents

All reagents were prepared with analytical grade chemicals and details of these can be found in Table 1.

Chemicals

Table 1: List of chemicals

<u>Chemical</u>	<u>Molecular Formula</u>	<u>Atomic/Molecular Mass (u)</u>	<u>Supplier</u>
Copper (I) bromide	CuBr	143.45	Sigma Aldrich
Bathocuproinedisulfonic acid disodium salt	C ₂₆ H ₁₈ N ₂ Na ₂ O ₆ S ₂	564.54	Sigma Aldrich
Ethylenediamine	NH ₂ CH ₂ CH ₂ NH ₂	60.10	Sigma Aldrich
Aluminium	Al	26.98	Fisher Scientific
Copper	Cu	63.55	Fisher Scientific
Iron	Fe	55.85	Fisher Scientific
Nitric Acid	HNO ₃	63.01	-
Sodium Chloride	NaCl	58.44	Fisher Scientific
Sodium Acetate trihydrate	CH ₃ COONa	136.08	Fisher Scientific
Acetic Acid	CH ₃ CO ₂ H	60.05	-
Hydrochloric Acid	HCl	36.46	-
Nitrogen	N ₂	28.01	-
Sodium dihydrogen phosphate dihydrate	H ₆ NaO ₆ P	156.01	Fisher Scientific
Sodium Hydroxide	NaOH	40.00	-
Disodium Tetraborate	Na ₂ B ₄ O ₇ ·10H ₂ O	381.38	Fisher Scientific

Reagent water

Milli-Q water (Millipore 18.2 MΩ cm) was used for the preparation of reagents and standards.

Solutions

(i) *Acetic Acid, 0.1 mol L⁻¹*: 5 mL of a 2M acetic acid stock solution was diluted in a 100 mL volumetric flask using Milli-Q water, then filled to the mark.

(ii) *Sodium Acetate (trihydrate), 0.1 mol L⁻¹*: 1.36 g of sodium acetate was dissolved using Milli-Q water in a 100 mL volumetric flask, then filled to the mark.

(iii) *Sodium Phosphate (sodium dihydrogen phosphate dihydrate), 0.1 mol L⁻¹*: 0.390 g of sodium phosphate was dissolved using Milli-Q water in a 25 mL volumetric flask, and then filled to the mark.

(iv) *Sodium Hydroxide, 0.1 mol L⁻¹*: 10 mL of a 1M sodium hydroxide stock solution was diluted using Milli-Q water in a 100 mL volumetric flask, then filled to the mark.

(v) *Sodium Borate (disodium tetraborate), 0.1 mol L⁻¹*: 3.81 g of sodium borate was dissolved using Milli-Q water in a 100 mL volumetric flask, and then filled to the mark.

(vi) *Sodium Chloride, 1.0 mol L⁻¹*: 11.67 g of sodium chloride was acidified with ~2 mL of 0.1M HCl in a 200 mL volumetric flask, then dissolved in Milli-Q water, filled to the mark.

(vii) *Sodium Chloride, 0.7 mol L⁻¹*: 8.18 g of sodium chloride was dissolved in Milli-Q water in a 200 mL volumetric flask, and then filled to the mark.

(viii) *Bathocuproine, 1x10⁻² mol L⁻¹*: 0.113 g of Bathocuproinedisulfonic acid disodium salt was dissolved in Milli-Q in a 20 mL volumetric flask, and then filled to the mark.

(ix) *Ethylenediamine, 5x10⁻⁵ mol L⁻¹*: 33 µL of ethylenediamine was diluted using a N₂ purged 0.7M NaCl solution in a 50 mL volumetric flask. 250 µL of this solution was diluted using a N₂ purged 0.7M NaCl solution in a 50 mL volumetric flask, and then filled to the mark.

Calibration standards

For the ICP-MS analysis of rainwater, 1,000 mg L⁻¹ stock solutions of Al, Cu and Fe were used to prepare the multi-element calibration standards. A blank and standards with concentrations of 3.0 µg L⁻¹, 2.5 µg L⁻¹, 2.0 µg L⁻¹, 1.5 µg L⁻¹, 1.0 µg L⁻¹ and 0.5 µg L⁻¹ of each element were made up. 250 µL of each element's 1,000 mg L⁻¹ stock solution was transferred into a 25 mL volumetric flask and made up using 2% nitric acid. 25 µL of this 10 mg L⁻¹ solution was diluted using 2% nitric acid in a 25 mL volumetric. From this 10 µg L⁻¹ solution, the following dilutions were made using the following method:

$$10 \mu\text{g L}^{-1} \quad \frac{7.50 \mu\text{L}}{25 \text{ mL}} \quad 3.0 \mu\text{g L}^{-1}$$

Table 2 shows the dilutions and concentration for all the multielement standards.

Table 2: Multielement ICP-MS calibration standards

Volume of 10 µg L⁻¹ multielement standard (µL)	Total Al, Cu, Fe concentration (µg L⁻¹)
7.50	3.00
6.25	2.50
5.00	2.00
3.75	1.50
2.50	1.00
1.25	0.50
0.00	0.00
<i>All standards made up to the mark using 2% Nitric Acid in 25 mL volumetric flasks 2% nitric acid was used as the blank.</i>	

Due to poor results for the Fe in the multi-element calibration standards, separate calibration standards were made up for the Fe. Table 3 shows the dilutions and concentration for the Fe stocks and standards.

Table 3: Fe ICP-MS calibration standards

Label	Volume of 1,000 mg L⁻¹ Stock (µL)	Volume of 10 mg L⁻¹ Fe Stock (µL)	Volume of 20 µg L⁻¹ Standard (mL)	Fe concentration (µg L⁻¹)
10 mg L ⁻¹ Fe Stock Solution	250.0	0.00	0.00	10,000
Standard 1	0.00	50.0	0.00	20.0
Standard 2	0.00	25.0	0.00	10.0
Standard 3	0.00	0.00	6.25	5.00
Standard 4	0.00	0.00	2.50	2.00
Standard 5	0.00	0.00	0.00	0.00
<i>All standards made up to the mark using 2% Nitric Acid in 25 mL volumetric flasks. 2% nitric acid was used as the blank.</i>				

These standards improved both the accuracy and precision of results for the Fe readings.

For the UV-Vis spectrophotometric analysis of Cu(I), Cu(I)Br was used to make up a 1×10^{-2} mol L⁻¹ Cu(I) standard from which aliquots were taken and diluted to give standard concentrations of 8×10^{-3} , 6×10^{-3} , 4×10^{-3} , 2×10^{-3} and 1×10^{-3} mol L⁻¹ Cu(I). Prior to use all volumetric flask were purged with N₂. 0.144 g of Cu(I)Br was diluted in a N₂ purged 1M NaCl (acidified) solution in a 100 mL volumetric flask. The flask was then placed in a warm water ultrasonic bath to aid dissolution. From this 1×10^{-2} mol L⁻¹ Cu(I) standard the following standards were made according to the dilutions shown in Table 4 were made.

Table 4: CuBr UV-Vis calibration standards dilutions

Volume of 1×10^{-2} mol L⁻¹ standard (mL)	CuBr concentration (mol L⁻¹)
8.00	8×10^{-3}
6.00	6×10^{-3}
4.00	4×10^{-3}
2.00	2×10^{-3}
1.00	1×10^{-3}
0.00	0.00
<i>All standards made up to the mark using 1M NaCl (acidified) in 10 mL volumetric flasks. 1M NaCl (acidified) used as the blank.</i>	

Sampling and sample preparation

Rainwater and roof run-off samples were collected at ground level in Plymouth, UK (50°23'22.9"N, 4°06'13.7"W) between 20th September and 25th October 2013. Samples were collected using 25 L polypropylene (PP) containers. Roof run-off was collected by positioning the PP container closely to a residential building funnelling

roof run-off rainwater into the container using a large PP funnel clamped in place. The containers were left constantly collecting until a sufficient volume was collected for analysis (~1 L minimum). The water samples were then transferred into 500 mL PP sample bottles. The sample bottles were stored in double zip-lock bagging and stored in a cool, dark area until analysis.

The analysis by ICP-MS was based upon EPA Method 200.8 (US EPA, 1994). No filtering of the samples was carried out as total copper concentration was under evaluation, not the total dissolved. Instead, prior to analysis via ICP-MS, both the rain and roof run-off water samples were acidified. This was performed by taking a 24 mL aliquot of the sample, and adding 1 mL of 70% HNO₃. Samples were then typically left for 15-20 minutes to digest before analysis.

Analytical procedure

Method validation by use of a certified reference material (CRM)

As an atmospheric water reference material was unavailable for the elements of interest in this experiment, a drinking water certified reference material 'EnviroMAT Drinking Water, Low (EP-L-3)' (supplied by SCP SCIENCE) was used during the analysis by ICP-MS. This allowed for the percentage recovery to be calculated, in turn allowing for the accuracy of the method to be assessed.

Table 5 shows the certified concentration for each element of interest, as well as their confidence interval.

Table 5: Certified concentrations for EnviroMAT Drinking Water, Low (EP-L-3)

Element	Consensus Value (mg L ⁻¹)	Confidence Interval
Al	0.100	0.0985-0.1015
Cu	0.0156	0.0153-0.0159
Fe	0.0279	0.0272-0.0285
N.B. Results after 1:1000 dilution		

The Confidence Interval has been calculated using the 95% Confidence Level (equivalent to 2σ) using Equation 3:

$$x \pm \frac{ts}{\sqrt{n}} \quad \text{Equation 3}$$

where n: Number of data

s: Standard Deviation of the Average

t: Factor for Student Test

x: Consensus value

Inert atmosphere procedure

The copper(I) ion is well noted to readily oxidise with oxygen in air when in solution. Any oxidation of the ion would therefore affect the results of the UV-Vis quantification. Therefore before use all glassware was purged with N₂ to eliminate as much oxygen as possible. All glassware was also sealed with Parafilm to provide an air-tight seal. Ethylenediamine was also noted to react with moisture in the air to form a hazardous, irritating mist. Elimination of air helped reduce loss as well as improve the safety of the experiment. All solutions were also purged with N₂ to reduce dissolved O₂ levels.

Effect of pH of Cu(I) complex stability

Moffett and Zika (1983) noted that the stability and absorptivity of the Cu(I) complex formed with bathocuproine was affected by the pH of the solution. To evaluate this, the same procedure was followed at three different pH levels. The pH of all solutions was checked with an Oakton pH6 Acorn Series meter, calibrated using pH 4.0 and 7.0 calibration solutions before each buffer measurement.

Each buffer was made up at 0.1M in a volumetric flask before checking the pH. The pH was then adjusted using a suitable solution until it fell in the required pH range. The buffer solution was then added to each Cu(I)Br calibration standard using a Pasteur pipette until their pH fell within the require pH range. Table 6 shows the pH ranges and adjusting solutions for each buffer solution.

Table 6: pH buffer volumes, adjustment solutions and ranges

<u>Buffer</u>	<u>Total Volume of Buffer (mL)</u>	<u>pH Adjustment Solution (0.1M)</u>	<u>pH range</u>
Sodium acetate	100	Acetic acid	5.6-6.0
Sodium phosphate	25	Sodium hydroxide	6.5-7.0
Sodium borate	100	Sodium hydroxide	>8.0

Instrumentation

Inductively Coupled Plasma-Mass Spectrometer

Aluminium, copper and iron concentrations in rainwater and roof runoff samples were determined using an inductively coupled plasma mass spectrometer (Thermo Scientific X Series 2 quadrupole ICP-MS Instrument). The operation parameters used for the instrument are shown in Table 7.

Procedure for multielement analysis by ICP-MS

The ICP-MS instrument and vacuum pumps were turned on prior to the make-up of the calibration standards. 10 mL volumetric flasks were filled and left to soak with 2% HNO₃ the day prior to analysis. The volumetric flasks were collected and emptied down the sink, and washed out once more using 2% HNO₃. A series of multielement (Al, Fe, Cu) calibration standards ranging 0-3.0 µg L⁻¹ were then made up following the dilutions shown in Table 3 using 5 mL, 1 mL and 250 µL automated pipettes. 24 mL of each Rainwater and Roof Runoff sample was pipetted in 50 mL beakers, and acidified with 1 mL of 70% HNO₃. Water samples were left to digest for 15-20

Table 7: pH Buffer volumes, Adjustment Solutions and ranges

Instrument	Thermo Scientific X Series 2
Forward Power (kW)	1.4
Coolant Gas Flow	13 L min ⁻¹ argon
Auxiliary Gas Flow	0.7 L min ⁻¹ argon
Nebuliser Gas Flow	0.86 L min ⁻¹ argon
Nebuliser Type	V-Groove
Spray Chamber Type	Sturman-Masters
Dwell Time (ms)	10
Sweeps	50
Collision Cell Gas	7% H in He introduced at flow rate of 3.5 mL min ⁻¹

minutes prior to analysis. Using a 1,000 mg L⁻¹ multielement standard the operation parameters of the ICP-MS instrument were calibrated until the optimal response for each element was achieved. The 2% HNO₃ solution was then ran through the ICP-MS instrument for ~5 minutes to ensure there was no contamination from previous samples. The lowest calibration standard (0.00 µg L⁻¹) was then run through the instrument for ~2 minutes before taking a measurement. The 2% HNO₃ blank was run through the instrument after each standard/sample to clear the instrument of the previous standard/sample. Each standard was measured from lowest to highest concentration following the same procedure. The 2% HNO₃ blank was then run through the instrument for ~5 minutes to ensure no residue standards were present. Each of the acidified rainwater and roof runoff samples were then measured following the same procedure. After each third sample, the 3.0 µg L⁻¹ multielement standard was measure to check for drift. Due to poor results for the Fe in the multielement calibrations, a series of Fe calibration standards were made up following the dilutions shown in Table 3. These were then measured following the same procedure as the multielement standards. Each of the acidified samples was then re-measured using the Fe calibration. The 2% HNO₃ blank was then run through the instrument for ~5 minutes. Three replicate measurements of the procedural blank was taken, as well as five replicate measurements of the acidified 'Roof Runoff 1' sample so the limit of detection and repeatability of the procedure could be evaluated.

UV-Visible Spectrophotometer

Copper (I) absorbance of the Cu(I)Br calibration standards were determined using an ultraviolet-visible spectrophotometer (Hewlett Packard 8453 diode array spectrophotometer). The operation parameters used for the instrument are shown in table 8.

Table 8: Operation parameters for UV-Vis spectrophotometer

Instrument	Agilent 8453 Single Beam Diode Array
Wavelength Range (nm)	250-900
Integration Time (secs)	0.5
Interval (nm)	1
Pathlength (cm)	1

Procedure for Cu(I) analysis by UV-Visible spectrophotometry

All volumetric flasks were washed using a Decon 90 and 10% v/v HCl bath prior to use. All masses were weighed out using an analytical balance. All volumetric flasks and Quikfit conical flasks were purged with N₂ for ~1 minute, sealed with Parafilm and stoppered prior to use. A 1M NaCl solution was made up in a 200 mL volumetric flask, acidifying with ~2 mL of 0.1M HCl before being made up to the mark using Milli-Q water. A 0.7M NaCl was made up in a 200 mL volumetric flask, with Milli-Q added up to the mark. The 0.7M NaCl solution was then placed under N₂ purge. Each buffer solution (sodium acetate, sodium phosphate, sodium borate) was made up at a concentration of 0.1M, making up to the mark with Milli-Q in a volumetric flask. 5 mL of a 2M acetic acid stock solution was diluted in a 100 mL volumetric flask using Milli-Q water, then filled to the mark. 10 mL of a 1M sodium hydroxide stock solution was diluted using Milli-Q water in a 100 mL volumetric flask, then filled to the mark. Monitoring the pH with an Oakton pH6 Acorn Series meter, the pH of each buffer solution was buffered using the appropriate adjustment solution until in the range shown in Table 6. A 1 x 10⁻²M bathocuproine standard was then made up in a 20 mL volumetric flask, made up to the mark using Milli-Q water. 100 µL and 500 µL microsyringes were cleaned out using the 0.7M NaCl solution. ~5 mL of ethylenediamine was transferred in a 25 mL beaker. A 1 x 10⁻²M ethylenediamine standard was made up in a 50 mL volumetric flask by transferring 33 µL of ethylenediamine using a 100 µL microsyringe, making up to the mark using a 0.7M NaCl solution. This solution was then purged with N₂ for ~5 minutes. 250 µL of the 1 x 10⁻²M ethylenediamine standard was then syringed into a 50 mL volumetric flask, made up to the mark using 0.7M NaCl solution, giving a concentration of 5 x 10⁻⁵M. 1M NaCl solution was placed under N₂ purge. A 1 x 10⁻²M CuBr standard was made up in a 100 mL volumetric, using 1M NaCl to make up to the mark. The 1 x 10⁻²M CuBr standard was placed in a warm water ultrasonic bath to aid dissolution. A series of CuBr standards were then made up from the 1 x 10⁻²M CuBr standard, following the dilutions shown in Table 4. A 1 mL microsyringe was then cleaned using the 1M NaCl solution. 0.5 mL of each CuBr standard was then transferred into 10 mL volumetric flasks, being made up to the mark with the 1M NaCl solution, giving x20 dilutions. Two additional x20 diluted 6 x 10⁻³M CuBr standards were made up; one was purged with N₂ for ~5 minutes then, with one left open to the air. These standards were then left in a fumehood overnight to evaluate whether the time of analysis affected the absorbance seen. Each other diluted CuBr solution, as well as the bathocuproine and ethylenediamine solutions were then purged using N₂ for ~5 minutes. These along with the 1M NaCl standard was taken to the photodiode array instrument for analysis. The instrument was turned on and set to the operation parameters shown in Table 8. The quartz cuvette was washed several times with the 1M NaCl solution, before taking a measurement of the 1M NaCl solution for a blank reading. The cuvette was then rinsed once with the diluted 1 x 10⁻²M CuBr standard,

before using a 1 mL autopipette to transfer 1 mL of the diluted 1×10^{-2} M CuBr standard, 1×10^{-2} M bathocuproine standard, and 5×10^{-5} M ethylenediamine standard into the cuvette. The cuvette content was mixed using a N₂ filled balloon connected to a syringe prior to analysis. The procedure was repeated for each standard, from highest to lowest concentration. The open and closed 6×10^{-3} M CuBr standards were retrieved the following day and were analysed by UV-Vis spectrometry using the same procedure. To calculate the limit of detection for the instrument, 5 replicate measurements of 1M NaCl with 1 mL of the bathocuproine and ethylenediamine standards were taken.

Quality control

Procedural blanks were prepared and analysed throughout the preparation of samples as well as the analytical process to assess for contamination.

A calibration verification solution ($3.0 \mu\text{g L}^{-1}$ for multi-element, $20 \mu\text{g L}^{-1}$ for Fe rerun) was included at the beginning and end of each ICP-MS run. An additional check was performed after every third sample analysed to check whether calibration drift was occurring. The verification concentration measured should fall within 10% of the expected concentration value.

Statistical analysis and calculations

The concentrations of Al, Fe and Cu in rainwater and roof runoff samples were obtained by ICP-MS automatically using the calibration standard measurements. The repeatability of the method was assessed by performing 5 replicate measurements of the sample 'Roof Runoff 1'. Using these concentrations, the standard deviation and relative standard deviation percentage (%RSD) could be calculated and evaluated. The %RSD should not exceed 5%. The accuracy of the method was assessed using the percentage recovery found for the certified reference material EnviroMAT Drinking Water, Low (EP-L-3). The limit of detection and quantification was assessed using the blank absorbance from the ICP-MS measurement.

Repeatability calculations

The arithmetic mean (\bar{x}) of the concentration determined with the replicate measurements was calculated using Equation 4: -

$$\bar{x} = \frac{\sum x_i}{n} \quad \text{Equation 4}$$

Where $\sum x_i$ is the sum of all replicate measurements
 n is the number of replicate measurements

The standard deviation (σ) of the replicate measurements was calculated using Equation 5: -

$$\sigma = \sqrt{\sum_i (x_i - \bar{x})^2 / (n - 1)} \quad \text{Equation 5}$$

Where σ is the standard deviation of the replicate measurements
 \bar{x} is the arithmetic mean of the replicate measurements
 Σx_i is the sum of all replicate measurements
 n is the number of replicate measurements

The relative standard deviation (%RSD) of the replicate was calculated using Equation 6: -

$$\%RSD = \frac{\sigma}{\bar{x}} \times 100\% \quad \text{Equation 6}$$

Where %RSD is the relative standard deviation of the replicate measurements
 σ is the standard deviation of the replicate measurements
 \bar{x} is the arithmetic mean of the replicate measurements

Accuracy calculations

The percentage recovery of Al, Cu and Fe of the certified reference material was calculated using Equation 7: -

$$\text{Recovery of Element of CRM (\%)} = \frac{\text{Conc. of element calculated } (\mu\text{g L}^{-1})}{\text{Conc. of element certified } (\mu\text{g L}^{-1})} \times 100\% \quad \text{Equation 7}$$

Limit of detection (LOD) and limit of quantification (LOQ)

The limit of detection of the analytical method can be defined as the lowest quantity of a substance that can be distinguished from the absence of that substance (a blank value) within a stated confidence limit (usually 1%) (MacDougall & Crummett, 1980). LOD is calculated by the sum of the mean signal intensity of the calibration blank and three times the standard deviation of the mean blank signal intensity (Miller & Miller, 2005).

$$\text{LOD} = y_B + 3 \cdot \sigma_B \quad \text{Equation 8}$$

The limit of quantification of the analytical method can be defined as the lowest quantity of a substance that can be reliably quantified. LOQ is calculated by the sum of the mean signal intensity of the calibration blank and ten times the standard deviation of the mean blank signal intensity.

$$\text{LOQ} = y_B + 10 \cdot \sigma_B \quad \text{Equation 9}$$

Results and Discussion

Results for Al, Cu and Fe concentrations by ICP-MS

In this section, the results of the rainwater and roof runoff samples measurements by ICP-MS were evaluated, as well as the accuracy, repeatability, and both the limit of detection and quantification of the analytical method.

Table 9: Determination of Al and Cu by ICP-MS results

Sample	Mean concentration ($\mu\text{g L}^{-1}$)		Standard Deviation, σ ($\mu\text{g L}^{-1}$)		%RSD	
	Al	Cu	Al	Cu	Al	Cu
Blank	0.118	0.00196	0.0499	0.00117	42.3	59.7
Standard 1	1.27	0.488	0.186	0.0150	14.6	3.07
Standard 2	3.84	1.16	0.570	0.0620	14.9	5.33
Standard 3	1.64	1.56	0.177	0.0260	10.8	1.66
Standard 4	1.88	2.03	0.454	0.0550	24.2	2.71
Standard 5	2.58	2.32	0.649	0.0310	25.13	1.33
Standard 6	2.95	3.05	0.183	0.0690	6.21	2.27
Rainwater 1	1.12	2.98	0.399	0.0260	35.5	0.872
Rainwater 2	0.253	2.00	0.293	0.0240	115	1.20
Rainwater 3	1.21	2.22	0.423	0.0590	35.0	2.66
Rainwater 4	2.61	2.03	0.729	0.0980	27.9	4.82
Rainwater 5	0.569	2.28	0.500	0.0110	87.9	0.482
Rainwater 6	-	1.60	-	0.0310	-	1.94
Roof Runoff 1	42.7	2.83	0.833	0.0400	1.95	1.42
Roof Runoff 2	44.9	3.54	0.668	0.0560	1.49	1.58
CRM	100.0	12.1	1.66	0.249	1.66	2.06

N.B. Cells containing a dash were below the limit of detection.

Table 10: Determination of Fe by ICP-MS results

Sample	Mean concentration ($\mu\text{g L}^{-1}$)	Standard Deviation, σ ($\mu\text{g L}^{-1}$)	%RSD
Blank	0.00214	0.00143	66.6
Standard 1	2.07	0.0900	4.35
Standard 2	5.04	0.0760	1.51
Standard 3	9.94	0.0460	0.463
Standard 4	20.0	0.453	2.26
Rainwater 1	1.82	0.0520	2.86
Rainwater 2	1.74	0.100	5.75
Rainwater 3	1.84	0.0370	2.02
Rainwater 4	1.93	0.201	10.4
Rainwater 5	1.74	0.0810	4.67
Rainwater 6	1.59	0.0600	3.78
Roof Runoff 1	2.80	0.218	7.78
Roof Runoff 2	2.83	0.315	11.1
CRM	24.3	0.331	1.36

Table 11: Rainwater sample concentrations by ICP-MS results

Element	Rainwater Sample Concentration ($\mu\text{g L}^{-1}$)						Mean Concentration ($\mu\text{g L}^{-1}$)
	1	2	3	4	5	6	
Al	1.12	0.163	1.21	2.61	0.569	-	1.14 ± 0.929
Cu	2.98	2.00	2.22	2.03	2.28	1.60	2.19 ± 0.456
Fe	1.82	1.74	1.84	1.93	1.74	1.59	1.78 ± 0.118

Table 12: Roof runoff sample concentrations by ICP-MS results

Element	Roof Runoff Sample Concentration ($\mu\text{g L}^{-1}$)		Mean Concentration ($\mu\text{g L}^{-1}$)
	1	2	
Al	42.7	44.9	43.8 ± 1.57
Cu	2.83	3.54	3.18 ± 0.506
Fe	2.80	2.83	2.81 ± 0.0163

Tables 9 and 10 show the concentrations of Al, Cu and Fe determined by ICP-MS for the calibration standards and CRM, as well as the rainwater and roof runoff samples. Tables 11 and 12 show the determined average concentration of the rainwater and roof runoff samples. Aluminium concentrations showed poor repeatability in both the calibration standards and rainwater samples, having high %RSD values, ranging from 6.21-115%. This is largely a result of aluminium concentrations being very low in atmospheric waters. The solubility of Al in rainwater has also been recorded to vary greatly between samples, being as low as 5% (Lim *et al.*, 1994). Due to the poor repeatability (>5%) and low concentrations, the values obtained for Al in the samples were deemed unacceptable for enrichment factor calculations in regards to Cu. Overall the %RSD values for the Cu and Fe standards were acceptable (<5%). The high %RSD values calculated for the procedural blanks for Cu and Fe were expected due to the small variance at low concentrations. Standard 2 was greater than the acceptable variance of 5% (5.33%), and therefore should have been omitted or remade.

Table 11 shows the mean concentration of Cu and Fe in rainwater samples was found to be $3.18 \pm 0.506 \mu\text{g L}^{-1}$ and $2.81 \pm 0.0163 \mu\text{g L}^{-1}$, respectively. These fell in the same magnitude to the values for Cu and Fe of $0.616\text{-}1.78 \mu\text{g L}^{-1}$ and $\leq 2.78 \mu\text{g L}^{-1}$ stated in Witt and Jickells (2005) and Montoya-Mayor *et al.* (2013), respectively. Table 13 shows the mean concentration of Cu and Fe in roof runoff samples was found to $3.18 \pm 0.506 \mu\text{g L}^{-1}$ and $2.81 \pm 0.0163 \mu\text{g L}^{-1}$, respectively. The value for Cu can be deemed relatively low, considering Odnevall Wallinder *et al.* (2009) stated a concentration range of $2\text{-}175 \mu\text{g L}^{-1}$.

Although only a small increase, the concentrations of Cu and Fe found within the roof runoff samples was higher than that of the rainwater samples. This is likely due to Cu and Fe particulate matter accumulating overtime upon the roofing in between rain events. Due to the sampling area being a residential area, automobile traffic is likely a large contributor to the concentrations found, as it accounts for ~65% of total Cu emissions in the UK (Kieber *et al.*, 2004). Geologically, the Devon area was well

known of having vast arsenic-copper deposits, such as those at the abandoned Devon Great Consols Mine (Palumbo-Roe, Klinck & Cave, 2007). Deposits of chalcopyrite (CuFeS_2) may contribute to copper and iron levels found in the Devon area.

The concentrations measured for rainwater and roof runoff samples needed considerations in relation to the toxicity upon phytoplankton. The measured copper concentrations of 2.19 ± 0.456 and $3.18 \pm 0.506 \mu\text{g L}^{-1}$ for rainwater and roof run off was very close/over the concentration of $2.56 \mu\text{g L}^{-1}$ which showed a 10% reduction in population for phytoplankton (Perez et al., 2010). This means further research and actions may need to be performed to assess this in greater detail. In many examples, the required concentration of Cu to be toxic to species was in the mg L^{-1} range (Chakraborty et al., 2010; Thit, Selck & Bjerregaard, 2013).

LoD and LoQ calculations for ICP-MS

Table 13: Procedural blank measurements by ICP-MS results

Element	Blank Concentration Reading ($\mu\text{g L}^{-1}$)					Mean Concentration ($\mu\text{g L}^{-1}$)	Standard Deviation, σ ($\mu\text{g L}^{-1}$)	%RSD
	1	2	3	4	5			
Al	0.0590	0.119	0.178	0.155	0.0790	0.118	0.0499	42.3
Cu	0.00	0.00200	0.00211	0.00300	0.00267	0.00196	0.00117	59.7
Fe	0.00	0.00207	0.00222	0.00400	0.00241	0.00214	0.00143	66.6

Table 14: Limit of detection and quantification calculations for ICP-MS

Element	Mean Concentration ($\mu\text{g L}^{-1}$)	Standard Deviation, σ ($\mu\text{g L}^{-1}$)	3σ	10σ	LoD ($\mu\text{g L}^{-1}$)	LoQ ($\mu\text{g L}^{-1}$)
Al	0.118	0.0499	0.150	0.499	0.268	0.617
Cu	0.00180	0.00110	0.00329	0.0110	0.00509	0.0128
Fe	0.00200	0.00141	0.00424	0.0141	0.00624	0.0161

Table 13 shows the concentrations for Al, Cu and Fe for five replicate measurements of the procedural blank. Table 14 summarises the calculated limits of detection and quantification of each element using Equations 8 and 9. The method limit of detection for Al, Cu, and Fe were calculated as 0.268, 0.00509 and 0.00624 $\mu\text{g L}^{-1}$, respectively. The method limit of quantification for Al, Cu, and Fe were calculated as 0.617, 0.0128 and 0.0161 $\mu\text{g L}^{-1}$, respectively.

Repeatability and accuracy calculations for ICP-MS

Table 15: Repeatability calculations for ICP-MS

Element	Concentration Reading ($\mu\text{g L}^{-1}$)					Mean Concentration ($\mu\text{g L}^{-1}$)	Standard Deviation, σ	%RSD
	1	2	3	4	5			
Cu	2.964	2.825	2.908	2.920	2.908	2.905	0.0503	1.73

Table 16: Accuracy calculations for ICP-MS

Element	Measured Concentration ($\mu\text{g L}^{-1}$)	Consensus Concentration ($\mu\text{g L}^{-1}$)	Percentage Recovered (%)
Al	100.0	100	100
Cu	12.1	15.6	77.6
Fe	24.3	27.9	87.1

Table 17: T-Test for rainwater and roof runoff for ICP-MS data

Sample	Cu Concentration ($\mu\text{g L}^{-1}$)	
	Rainwater	Roof Run Off
1	2.98	2.83
2	2.00	3.54
3	2.22	-
4	2.03	-
5	2.28	-
6	1.60	-
Two-tailed P value	0.164	
Level of Significance	0.05	

Table 15 shows the method repeatability, calculated using Equation 6, whereas Table 16 shows the method accuracy, calculated using Equation 7. The repeatability was calculated using five replicate measurements of 'Roof Runoff 1'. The %RSD was found to be 1.72%, showing the overall precision of the method was acceptable. The accuracy was calculated using the CRM 'EnviroMAT Drinking Water, Low (EP-L-3)' as a percentage recovery of the certified value. The percentage recoveries for Al, Cu and Fe were found to be 100, 77.6 and 87.1%, respectively. EPA Method 200.8 (US EPA, 1994) states the percentage recovery of copper should fall within 94-107%. As the result of 77.6% falls outside this range the method accuracy is unacceptable for quantifying Cu accurately. There are several possible causes for the poor accuracy. The operation parameters of the ICP-MS instrument may not have been optimised for Cu due to Al and Fe being present in the standard used to calibrate. The Al in the multi-element calibration standards may have inhibited the response of the Cu, and therefore standalone Cu calibration standards would be recommended. It is also possible that the acidification of the samples and CRM was

not sufficient. Analysis was carried out ~20 minutes after acidification, whereas EPA Method 200.8 recommends waiting 16 hours after acidification to analyse. As a result the complexed Cu content within the sample matrix may not have been fully decomposed, meaning the total Cu content was not determined. Table 17 shows a two-tailed t-test performed between the rainwater and roof runoff samples in order to determine whether the Cu concentration could be seen to differ statistically. As the P value of 0.164 was greater than the level of significance at 0.05, it could be stated that statistically the concentrations of Cu in the rainwater and roof runoff cannot be differentiated.

Results for Cu(I) concentrations by UV-Visible spectrometry

In this section, the UV-Visible method for determining Cu(I) concentration by complexing with bathocuproine was evaluated using data obtained for Cu(I)Br standards. The effect of pH on the absorbance, as well as the oxidation and time between measurements of the complex was evaluated. The limit of detection and quantification of the analytical method were also calculated. The characteristic absorbance maxima for the Cu(I) bathocuproine complex was at 480 nm in the UV-Visible spectrum (Ahmed Syed & Syeda, 2007). Unlined standards shown in these tables were omitted from the calibration plots as they showed poor results. The noise seen from 250--~375 nm in the spectra was likely due to the solvent (1M NaCl acidified with 0.1M HCl) or the quartz cuvette.

Table 18: UV-Visible spectrophotometer absorbance readings at 480 nm for CuBr standards at pH 5.6

Standard Name	True Concentration (mM)	Absorbance (AU)
Blank	0.00	0.0457
1 x 10 ⁻³ M x20 dilution	0.0500	0.0792
2 x 10 ⁻³ M x20 dilution	0.100	0.0945
4 x 10 ⁻³ M x20 dilution	0.200	0.144
6 x 10 ⁻³ M x20 dilution	0.300	0.179
8 x 10 ⁻³ M x20 dilution	0.400	0.215
<u>1 x 10⁻²M x20 dilution</u>	<u>0.500</u>	<u>0.223</u>
Calibration Line Equation = 0.416x +0.0535		
R ² = 0.992		

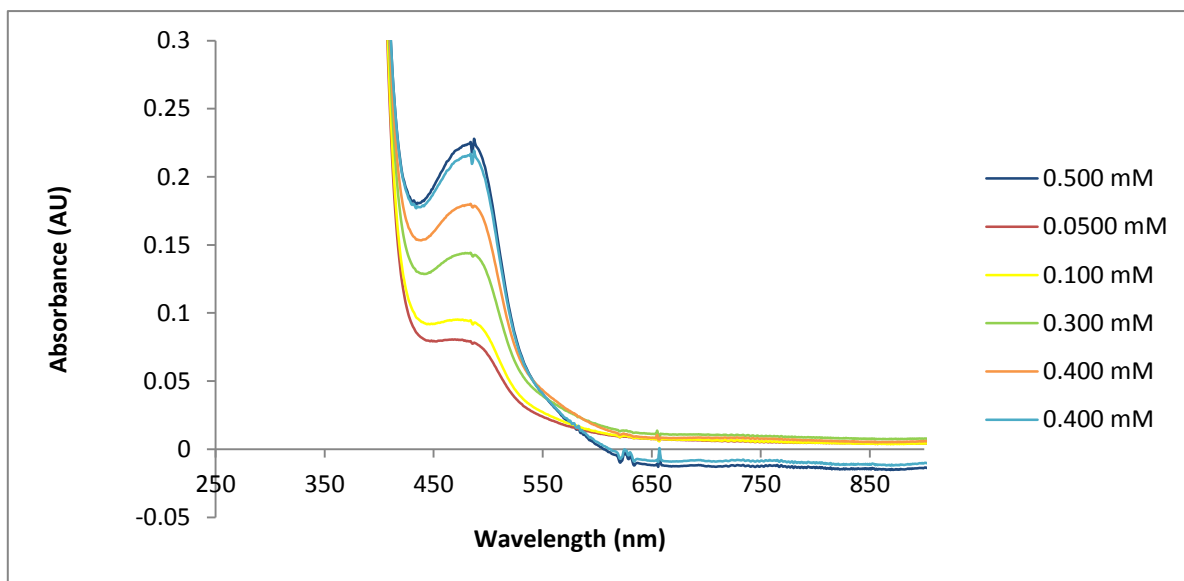


Figure 2: UV-Visible spectrum for Cu(I) bathocuproine complex at pH 5.6

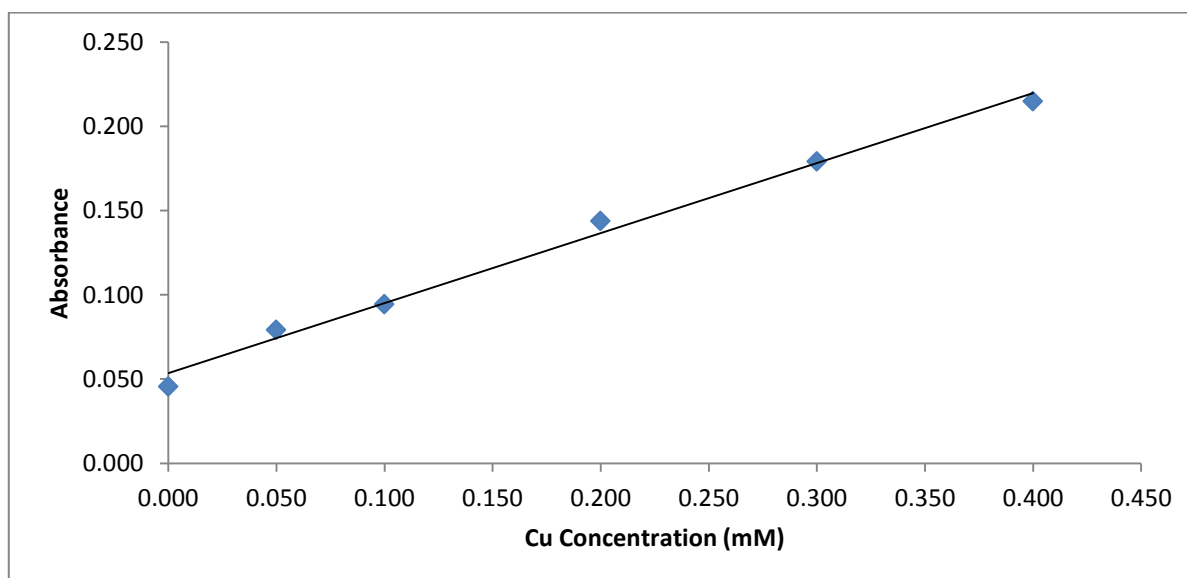


Figure 3: Calibration plot for 480 nm absorbance of Cu(I) bathocuproine complex at pH 5.6

Table 18 shows the absorbance results for each CuBr standard at pH 5.6, with Figure 2 showing the UV-Visible spectrum zoomed in at the 480 nm absorbance. Figure 3 shows the calibration plot at pH 5.6.

Table 19 shows the absorbance results for each CuBr standard at pH 6.5, with figure 4 showing the UV-Visible spectrum zoomed in at the 480 nm absorbance. Figure 5 shows the calibration plot at pH 6.5.

Table 19: UV-Visible spectrophotometer absorbance readings at 480 nm for CuBr standards at pH 6.5

Standard Name	True Concentration (mM)	Absorbance (AU)
Blank	0.00	0.0458
1 x 10 ⁻³ M x20 dilution	0.0500	0.0829
2 x 10 ⁻³ M x20 dilution	0.100	0.0909
4 x 10 ⁻³ M x20 dilution	0.200	0.128
6 x 10 ⁻³ M x20 dilution	0.300	0.207
8 x 10 ⁻³ M x20 dilution	0.400	0.265
<u>1 x 10⁻²M x20 dilution</u>	<u>0.500</u>	<u>0.453</u>
Calibration Line Equation = 0.535x + 0.0431		
R ² = 0.978		

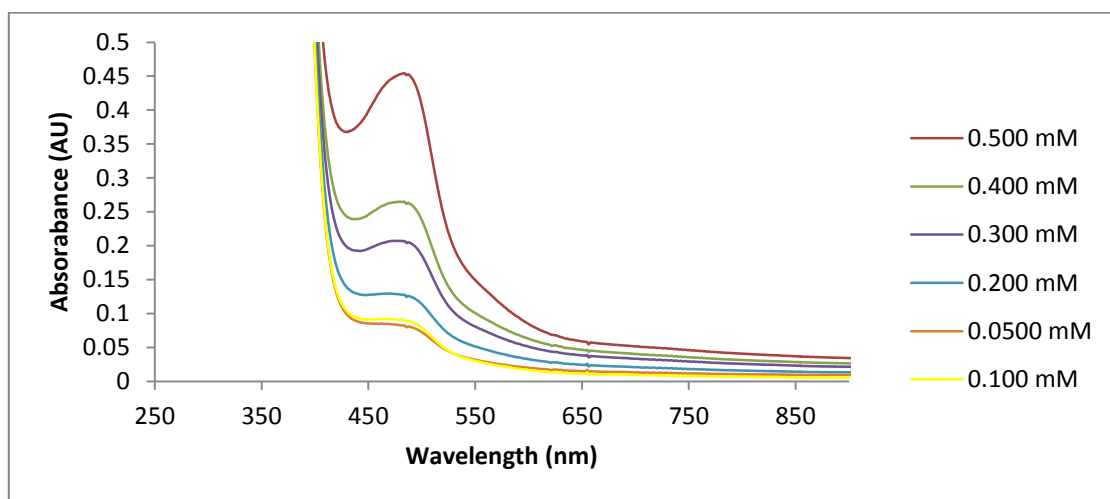


Figure 4: UV-Visible spectrum for Cu(I) bathocuproine complex at pH 6.5

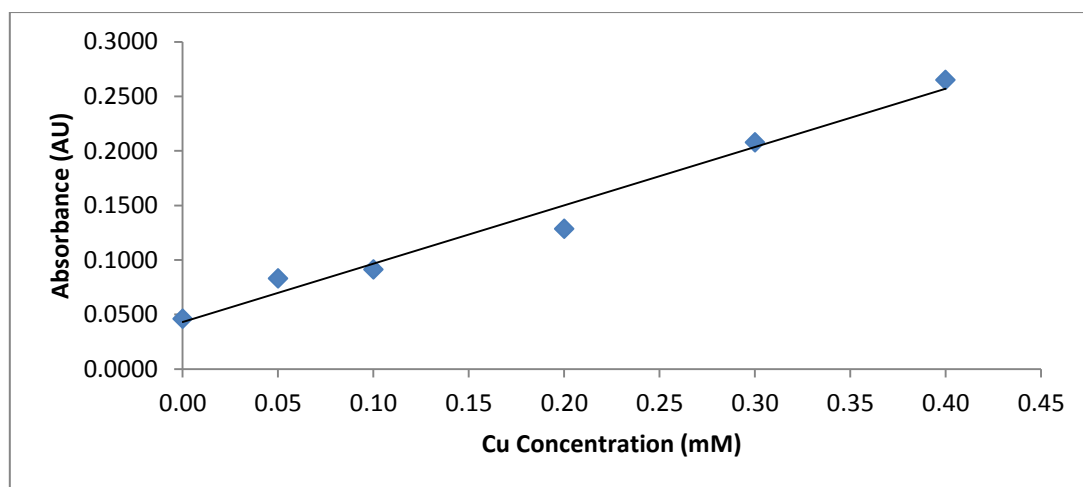


Figure 5: Calibration plot for 480 nm absorbance of Cu(I) bathocuproine complex at pH 6.5

Table 20: UV-Visible spectrophotometer absorbance readings at 480 nm for CuBr standards at pH >8.0

Standard Name	True Concentration (mM)	Absorbance (AU)
Blank	0.00	0.0460
1 x 10 ⁻³ M x20 dilution	0.0500	0.0857
2 x 10 ⁻³ M x20 dilution	0.100	0.108
4 x 10 ⁻³ M x20 dilution	0.200	0.138
6 x 10 ⁻³ M x20 dilution	0.300	0.188
8 x 10 ⁻³ M x20 dilution	0.400	0.296
1 x 10 ⁻² M x20 dilution	0.500	0.371
Calibration Line Equation = 0.622x + 0.0385		
R ² = 0.966		

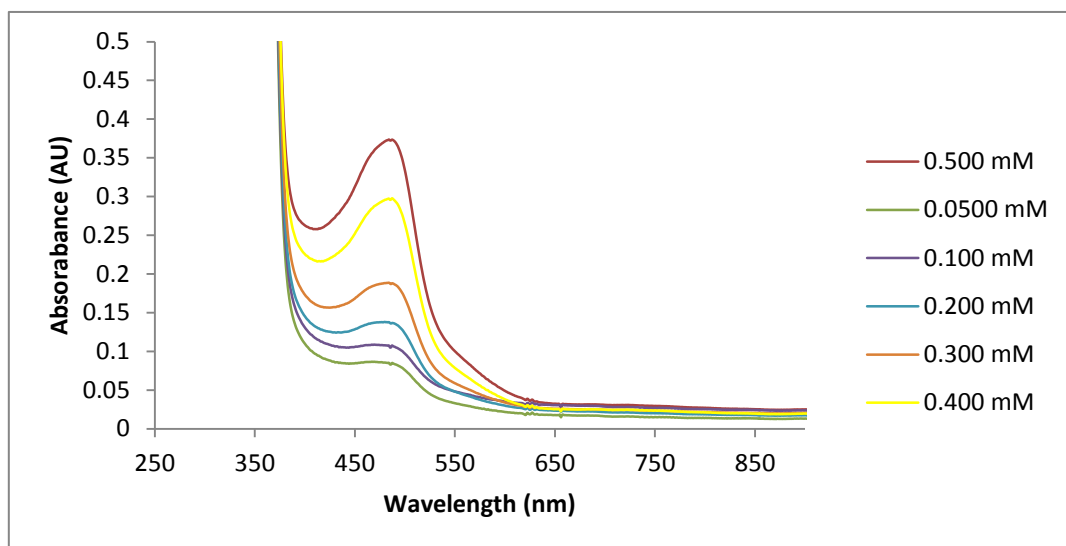


Figure 6: UV-Visible spectrum for Cu(I) bathocuproine complex at pH >8.0

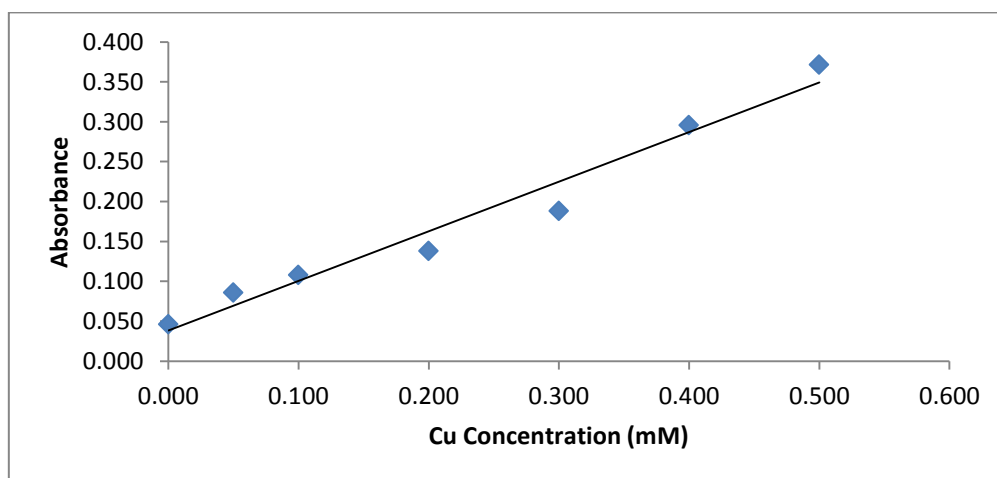


Figure 7: Calibration plot for 480 nm Absorbance of Cu(I) bathocuproine complex at pH >8.0

Table 20 shows the absorbance results for each CuBr standard at pH >8.0, with Figure 6 showing the UV-Visible spectrum zoomed in at the 480 nm absorbance. Figure 7 shows the calibration plot at pH >8.0.

The absorbance readings at all pHs, as well as the calibration line Equations for each calibration plot shows that the relationship between Cu(I) concentration and absorbance at 480 nm does not have a simple ratio, e.g. double the concentration, double the absorbance. The pH was seen to directly affect the absorbance measured for equal concentrations. The higher the pH (i.e. more basic), the higher the absorbance read. This is likely due to the stability of the Cu bathocuproine complex being poor below pH 6; absorbance decay was noted by Moffett and Zika (1983), resulting from proton exchange of the Cu(I) in the complex, followed by Cu(I) oxidation. It also stated that in a seawater sample the complex remained stable for over an hour at pH values near 8.

Some minor absorbance was seen in each spectra around ~630 nm, characteristic of the absorbance maxima for $[\text{Cu}(\text{en})_2]^{2+}$ (Song *et al.*, 2005). This could indicate the ethylenediamine was effectively masking any Cu(II) interference upon the Cu(I).

UV-Visible spectrometry calibration results

The coefficient of determination (R^2) for the calibration plots at pH 5.6, 6.5 and >8.0 (Figures 3, 5 and 7) were calculated as 0.992, 0.978 and 0.965. Overall this indicated strong linear correlations between the concentration and absorbance. For the pH 5.6 and 6.5 standards the absorbance for 1×10^{-2} M x20 diluted standards were omitted as the results were poor. For the pH 6.5 standards, the 1×10^{-3} and 4×10^{-3} M x20 diluted standards fell either side of the trend line, suggesting errors in the concentrations. Omitting these gave a more positive R^2 value of 0.9981. Similarly for the pH >8.0 standards, the 4×10^{-3} and 6×10^{-3} M x20 diluted standards fell below side of the trend line. Omitting these gave a more positive R^2 value of 0.9985. These possible errors in concentration are likely a result of the makeup of the calibration standards. Due to the several dilution steps, errors can be easily introduced. To improve upon these results, it would be recommended to remake the calibration standards with fewer dilution steps, and using automated pipettes rather than the graduated pipettes used.

Oxidation of Cu(I) and 24 hour passing measurement results

Table 21: UV-Visible spectrophotometer absorbance readings at 480 nm for 6×10^{-3} M CuBr opened and closed system standards at pH 5.6 measured after 24 Hours

Standard	Absorbance (AU)
Closed	0.272
Open	0.254

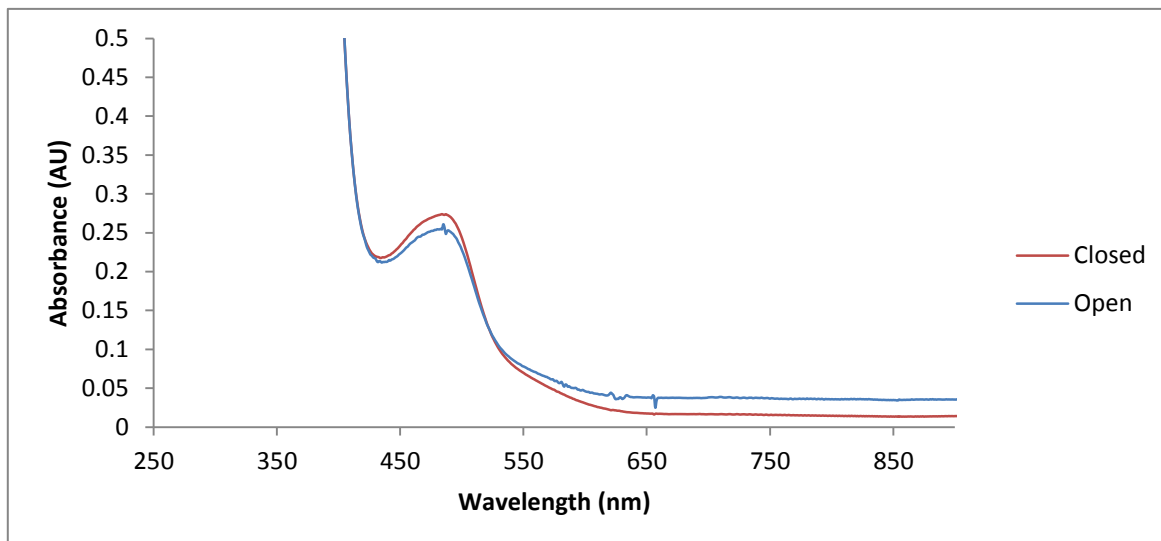


Figure 8: UV-Visible spectrum for 6×10^{-3} M Cu(I) bathocuproine complex at pH 5.6 after 24 hours for Opened and Closed Systems

Table 21 shows the absorbance results after 24 hours for an opened and closed 6×10^{-3} M $\times 20$ dilution CuBr standards at pH 5.6. Figure 8 show the UV-Visible spectrum zoomed at the 480 nm absorbance, respectively. The absorbance for the closed and open systems was 0.272 and 0.254 AU, respectively, compared to the absorbance of 0.179 AU seen for the immediate measurement of the standard (Table 18). The higher absorbance readings for the 24 hour measurements are likely a result of errors in the standard concentrations, as lower absorbance readings are expected due to oxidation and loss of stability over time of the complex. The absorbance does however suggest that the stability of the complex is greater than that suggested by Moffett and Zika (1983), still showing high readings an entire day after makeup of the solution. The opened system did show a small reduction in absorbance to that of the closed system. This would indicate partial oxidation of the Cu(I) concentration. Sharma & Millero (1988) observed a $t_{1/2}$ of 1.30 minutes for Cu(I) in 1M NaCl at pH 8 and 25°C. The overall reduction in absorbance being small suggests the oxidation kinetics for Cu(I) in the presence of air is slower however. Moffett and Zika (1983) suggest Cu(I) has a sufficiently long lifetime, existing at steady levels in natural waters. The lifetime of the Cu(I) is a function of pH and complexing ligands present and redox intermediates such as H_2O_2 . They also suggest Cu(I) is stabilised in natural waters containing appreciable quantities of chloride ion. Chloride ions stabilise dissolved Cu(I) in the form of complex anions, such as $CuCl_2^-$ and $CuCl_3^{2-}$. As the CuBr standards were made up using 1M NaCl there was a considerable Cl⁻ concentration in solution. Deng (1998) observed chloride concentrations ranging from 5.0–200 μ M in rainwater samples in Florida, likely originating from marine aerosol. As the sampling location of Plymouth, UK is a coastal city, it is likely the rainwater sample contains chloride, resulting in the stability of the Cu(I) species.

Method limit of detection, quantification and repeatability for UV-Visible spectrometry

Table 22: Limit of detection and quantification calculations for UV-Visible spectrophotometer

Absorbance (AU)					Mean Absorbance (AU)	Standard Deviation, σ (AU)	%RSD
1	2	3	4	5			
0.0457	0.0458	0.0460	0.0458	0.0460	0.0458	1.25×10^{-4}	0.273

3σ (AU)	10σ (AU)	Limit of Detection (mol L^{-1})	Limit of Quantitation (mol L^{-1})
3.76×10^{-4}	1.25×10^{-3}	1.11×10^{-4}	1.13×10^{-4}

The method limit of detection and quantification for Cu(I) was calculated to be 1.11×10^{-4} and 1.13×10^{-4} M, respectively (Table 22). This was two magnitudes higher than the value of 1×10^{-6} M states in Moffett and Zika (1983). This may be a result of the operation parameters differing between the method, or possibly inaccuracies in the CuBr standard concentrations. The purities of the bathocuproine may have also had an effect on the measured absorbance. As a result of the calculated limit of detection, the method is unsuitable for the determination of Cu(I) in atmospheric waters, which has a concentration closer to 1×10^{-8} M.

The calculated % RSD for the blank replicate measurements was found to be 0.273. This illustrated that the method showed very good precise and repeatability.

Conclusions

The total mean concentrations of Al, Cu and Fe determined by ICP-MS for the rainwater samples were 1.14 ± 0.929 , 2.19 ± 0.456 , and $1.78 \pm 0.118 \mu\text{g L}^{-1}$, respectively. For the roof runoff samples they were determined to be 43.8 ± 1.57 , 3.18 ± 0.506 , $2.81 \pm 0.0163 \mu\text{g L}^{-1}$, respectively. These concentrations were close to or within the ranges stated in previous studies (Witt & Jickells, 2005; Odnevall Wallinder, Hedberg & Dromberg, 2009). Although the repeatability of the method showed good results at 1.73%, the accuracy of the method calculated with the CRM was overall rather poor, with a percentage recovery of only 77.6% for the copper, meaning the data obtained by ICP-MS was unreliable. The limit of detection was found to be $0.00509 \mu\text{g L}^{-1}$, close to two magnitudes lower than stated in EPA method 200.8 of $0.5 \mu\text{g L}^{-1}$ (US EPA, 1994). At the observed concentration of copper in both the rainwater and roof runoff samples, there are implications that need to be considered regarding its toxicity to phytoplankton.

The determination of Cu(I) by UV-Vis spectrophotometry using bathocuproine showed good results throughout each of the experimental conditions. The highest overall absorbance for the $[\text{Cu}(\text{BCP})_2]^+$ complex was seen at a pH over 8.0. This was likely due to an instability of the $[\text{Cu}(\text{BCP})_2]^+$ complex when below pH 6, resulting from the exchange of a proton for Cu(I), followed by the oxidation of Cu(I) (Moffett &

Zika, 1983). Positive results were seen for the calibration plot for each pH, showing a near-linear relationship between the absorbance and copper concentration. The $[\text{Cu}(\text{BCP})_2]^+$ complex solution that was left open overnight showed a small decrease in the measured absorbance compared to the closed system. This suggests the $[\text{Cu}(\text{BCP})_2]^+$ complex is quite stable, possibly a result of the chloride ions in solution. The limit of detection for the method was found to be 1.11×10^{-4} M, meaning the method is unsuitable for determining Cu(I) in atmospheric water samples. The method however is valid for other natural water samples, such as seawater.

Future Work

Ongoing from the results achieved from the procedures carried out throughout this project, several recommendations could be made if the procedures were to be repeated. When acidified, the samples analysed by ICP-MS should have been left for a minimum of 16 hours as outlined in EPA Method 200.8 (US EPA, 1994). This could have given a more accurate result, as well as likely improving the percentage recovery for the CRM. The time between the rainwater and roof run off collection and analysis by ICP-MS could have been decreased, improving the composition of the samples and making them more representative. For the UV-Vis spectrometry analysis, the procedure could have been improved using automated pipettes to improve on the accuracy of the CuBr standard concentrations, as well as within a seal container such as a glove box under an inert atmosphere to help eliminate any oxidation of the Cu(I). More calibration standard concentrations could have also been made up to improve the calibration plot.

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