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Airborne Particulate Matter Sample Analysis Using Dried-Droplet Standards and Laser Ablation Inductively Coupled Plasma Mass Spectrometry

Master's Thesis in the International Master's Programme Environmental Measurement Techniques

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Abstract

Laser ablation inductively couple plasma mass spectrometry (LA-ICP-MS) has become a popular technique for direct analysis of trace elements in solids. It is however important that LA-ICP-MS analysis is performed together with adequate calibration in order to provide quantitative data. In this work, we developed a calibration strategy for the analysis of airborne particles collected on cellulose filters. The calibration was performed using dried droplets of multi-element standard solutions placed on a cellulose filter. The size of the drop was measured and the density of trace elements was determined. The standards were analysed by LA-ICP-MS and the signal was related to element density. A series of 10 samples collected in Boston (USA) using a high volume PM10 impactor was then analysed.

In this report, the calibration strategy is explained and the performance of LA-ICP-MS for the analysis of air samples is tested. The method proved reliable for the analysis of trace metals in airborne particles.

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1. Introduction

Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) is a technique which offers the possibility to analyse major, minor and trace elements in solids. This technique is already well established in the geological fields with additional applications in other key areas, such as forensics, materials science, and medical and biological sciences as well as chemical analysis in general. (1) In LA-ICP-MS, a laser beam is used for direct solid sampling for online ICP-MS analysis, thereby solving many of the problems associated with the conventional acid-digestion method. The absence of sample preparation for LA-ICP-MS reduces the analysis time and minimises sample preparation, which make it especially attractive compared with the conventional ICP-MS analysis which requires sample digestion prior to analysis. However, LA-ICP-MS suffers from non- stoichiometric effects occurring during sampling, aerosol transport, vaporisation, atomisation and ionisation within the ICP, which is described as elemental fractionation. This matrix dependent phenomenon has been the limitation for quantitative analysis without matrix matched calibration standards. At present, a variety of methods are being developed for more precise and accurate quantitative analyses by LA-ICP-MS.

Finding a better way to prepare standards for analysing airborne particulate matter samples should enable rapid analysis with minimal sample contamination. A good calibration is critical for accurate and precise analysis. Several methods have been developed to prepare solid standards for air particle analysis. A method is to prepare filter standards with known amount of particles and element concentrations by depositing the standard urban particulates on the filter in a designed sampling chamber. (2) Calibration has also been performed using a standard filter prepared by dripping an aqueous standard solution on the filter. The real samples consist of particles on filters instead of material impregnated in filters. Therefore only semi-quantitative analysis is possible with a relative accuracy of about 10%. (3)

The major goal of this thesis work is to develop calibration of the LA ICP-MS for the analysis of airborne particulate samples. The idea is to drop a coloured standard solution onto blank filters which are of the same type as the sampling filter. The standard solutions are prepared in several different concentrations in order to obtain a slope for calibration. The solution should be dyed heavily enough to be illustrating on the filter. The colorant must be pure, which means that it should not contain significant amounts of the elements to be analysed. The drop size of the solution should be in an accurate volume and a small possible so that the spots on the filter would be small and circular, so that the standard solution dropped on the filter is homogenously distributed. This simplifies the calculation of the spots area as approximate circle and the estimation of the density of metals in the spot area. Details of the standard preparation are described in the methodology part. Using the drop size and the density of elements on the filters, it is possible to calibrate signals obtained from the ICP-MS. Subsequently, the metal levels in the air can be calculated for analysed air particle samples.

2. Background

2.1 The environment

The environment is a complex set of surroundings where the organization works, including air, water, land, natural resources, flora, fauna, humans and their interrelation. It can be the place where we live and work. It can be the atmosphere we breathe and water we drink. It can be an undiscovered area that is full of wild lives. It can be the sunshine that the plants use to grow. It can be any physical, geographic, biological, social, cultural and political condition that surround an individual or organism and that ultimately determines its form and nature of its survival. The environment is changing all the time. Physical forced continuously change the surface of the planet through weather, the action of tide and other natural phenomena like earth quake. Chemical reactions operate in the atmosphere produce ozone which protects us from the harmful ultraviolet radiation from the sun. Living organisms also play an important role by photosynthesis, respiration, assimilation and catabolism. As early as the beginning of the earth, the atmosphere began to change. The carbon dioxide concentration in the present air is much lower than hundreds of million years ago. It is warmer today than the ice age. The volcano eruption happens suddenly and brings gases, vapour and dust into the atmosphere. No matter it is the long term change or the short term, the species on the earth are strongly affected by the environment. Some species survived by evolution when the environment is changing, but many died out. Human is considered as one of the successful species on the earth. As the developing of the human society, the environment becomes greatly affected by human activities. Although the natural power is so strong that people can hardly avoid natural disasters such as solar flare and tsunami. However, negative artificial environmental effect is possible to avoid.

2.2 Environmental pollution

All the natural resources that people are using come from the environment. Through the industrial and agricultural processes these resources become either useful finished products such as gasoline and corn, or useless waste released back to the environment like exhaust gas and dust. Not only will the earth be depleted by its resources, with the inevitable environmental damage, but there will almost certainly be a parallel increase in waste produced and in pollution of the earth. Pollution means the introduction by man, directly or indirectly, of substances or energy into the environment resulting in deleterious effects of such a nature as to endanger human health, harm living resources or interfere with amenities or other legitimate use of the environment. (4) Pollution can be on different aspects. There is physical pollution like noise. Chemical pollutions are much more concerning because of the various pollutant and the effects on the environment. The pollutants are released into the

environment in many forms. For instance, carbon dioxide, used to be mainly from a product of respiration by the living organisms, its concentration in the atmosphere is increasing and primarily associate with global warming problem as a result of fuel combustion. This soluble gas may precipitate together with sulphur oxides and nitrogen oxides into rivers and lakes and cause the acidification problem. Heavy metals are contained in particles or solute in waste water. Many of them are related to human health problems. There are many more examples showing that problems occur by the release of the substances into the environment which are naturally present, the problem arising simply from an increase in concentration above "natural" levels. (4) To measure the pollutants in the environment, is for analysis, a better recognition and determine the extent of the problem, so that people can find ways to control them and make legislation to ensure the control procedures.

2.3 Air pollution

Air is a basic necessity of human's existence. It supplies people with oxygen which is essential for living. 99.9% of the air is nitrogen, oxygen, water vapour and inert gases. (5) However, while human's life quality is improving during the last century, the air quality becomes poorer, which could due to the substances released into the air through human activities. Some of them may cause problems to not only humans, but also plants and animals. The study of human health reminds public that human health is under attack by the contaminants that people breathe in. Commonly discussed, several main types of air pollution and well-known effects of pollution include smog, acid rain, the greenhouse effect, and ozone layer depletion. Each of these problems has serious implications for human health and well-being as well as for the whole environment. Some air pollutant can be explained in term of either natural or anthropogenic source activities. Others can be formed indirectly from chemical processes in the atmosphere. They are therefore distinguished into primary and secondary pollutants. The air pollutants are mainly either gaseous or particulates in nature. The gaseous type of pollution is the release of noxious gases, such as sulphur dioxide, carbon monoxide, nitrogen oxides, and chemical vapours. These can take part in further chemical reactions once they are in the atmosphere, for instance, forming smog and acid rain. The particulate type of air pollution is the release of particles into the air mainly coming from the burning fuel for the energy. Diesel smoke is a good example of this particulate matter. The exhaust from burning fuels in automobiles, homes, and industries is a major source of pollution in the air. Further more, the particles can be distinguished into fine and coarse particles. They have different source and formation mechanisms. Primary fine particles are formed from condensation of high temperature vapours during combustion. (6) Secondary particles are usually formed in three ways: The first way is that particles recently emitted from process or freshly formed within the atmosphere. They are in nucleation mode which is usually less than 0.2μm in diameter. The second way is accumulation mode particles that between 0.2 and 2μm in diameter growing from a nucleation mode by coagulation or condensation of vapours. The third way is by reaction of absorbed gas in liquid droplets. Chemical reactions of gases in the atmosphere can also form particles. They may either have a low enough pressure to from a particle or react further to form a low vapour substance. For

example, the conversion of SO_2 to H_2SO_4. (6) By contrast, most of the course fraction particles are formed directly as particles and, result from mechanical disruption such as grinding, crushing, sprays evaporation or suspension of dust from construction and agricultural operations. (6) The course particle size is normally greater than 1 μm in diameter owing to the energy consideration. Usually larger particles are unlikely to be inhaled and do not stay airborne for a long time. They deposit near their source. Smaller particles can travel for a longer distance and can be inhaled. Particulate matter less than 10 microns in diameter (PM10) are one of most common pollutants that are currently referred to.

2.3 Importance of measuring airborne contaminants

Human health is the most commonly concerned problem affected by air pollution. Furthermore, poor air quality may not only affect human health, but also damage the crops and material and degrade sensitive ecosystem. (6) The extent to which an individual is harmed by air pollution usually depends on three factors: the concentration and the component of the pollutant, the duration of exposure and the susceptibility of the sensitive receptors such as human, plants and animals.

Effects of air pollution can be in many ways with both short-term and long-term effects. Different groups of individuals are affected by air pollution in different ways. Some individuals are much more sensitive to pollutants than are others. Young and elderly often suffer more from the effects of air pollution. Weak people with health problems such as asthma, heart and lung disease may also suffer more in the polluted air.

Short-term effects of air pollution can be irritation of the eyes, nose and throat, and upper respiratory infections such as bronchitis and pneumonia. Other symptoms can include headaches, nausea, and allergic reactions. Short-term air pollution can aggravate the medical conditions of individuals with asthma and emphysema. In the great "Smog Disaster" in London in 1952, four thousand people died in a few days due to the high concentrations of pollution. (5) Long-term health effects can include chronic respiratory disease, lung cancer, heart disease, and even damage to the brain, nerves, liver, or kidneys. Continual exposure to air pollution affects the lungs of growing children and may aggravate or complicate medical conditions in the elderly people. (5)

Research into the health effects of air pollution is ongoing. Medical conditions arising from air pollution can be very expensive. Healthcare costs, lost productivity in the workplace, and human welfare impacts cost countless money each year.

As the concern of the environment has become increasingly important, the measurement techniques are developing constantly. Measuring atmospheric transport in the form of particulates is one of the major methods for knowing the disposal of the pollutants.

Particles vary in size or shape, chemical component, and they can be either solid particles or

liquid droplets. They are commonly divided into two groups by size: PM10 and PM2.5. PM10 are particles smaller than 10 micrometers in size. PM2.5 is particles smaller than 2.5 micrometers in size. PM10 include coarse particles which can comprise smoke, dirt and dust from factories, farming, and roads, spores, and pollen. They may be made from the erosion of rocks and soil and blown away by wind. PM2.5 are mainly fine particles which can include toxic organic compounds and heavy metals which may come from automobile emissions, biomass burning (bush fires and forest fires or yard waste burning), and smelting (purifying) and processing metals. Since the smaller particles are lighter and they stay in the air longer and travel farther. PM10 particles can stay in the air for minutes or hours while PM2.5 particles can stay in the air for days or weeks. PM10 particles can travel as little as a hundred meters or as much as tens of kilometre. PM2.5 particles go even farther; many hundreds of kilometre. In addition, fine particles present higher health and environmental risks because of deeper penetration into the lungs and higher surface area, respectively.

Concentrations of particles in the atmosphere are variable. High levels of particles can occur due to the natural facts like wind-blown dust from arid soil or human activities such as fires, mining, overgrazing or farming. In many cities the annual average concentration of PM10 are in the range 20-50 $\mu g/m^3$. (6) However, in the cities of some developing countries, the annual concentration of PM10 can be above 100$\mu g/m^3$. Concentrations of PM2.5 are usually about 45 to 65% of the concentrations of PM10. (6)

2.4 Measuring techniques for airborne particles

There are several ways to measure the airborne particles. Normally, the process of measuring the airborne particles is divided into 3 steps: sampling, pre-treatment/preparation of the sample and analysis as simply described in the **Figure 1**. Although some of the direct measurement techniques do not require any sample pre-treatment/preparation.

The first step is sampling and is usually performed by filtration from the atmosphere, in which high volume samplers are one of the major sampling methods; other methods include personal samplers and cascade impactors. In the high-volume samplers, the air sample is pumped through a large membrane filter (20-25cm) typically at 75m^3/h. The sampling time can range from an hour for contaminated urban air to 12 hours for clean rural air. The filter type can be chosen base on the retention of the correct size range, absence of trace impurities in the filter and compatibility with the subsequent analytical procedure some of which require the total combustion of the filter or its dissolution. Consideration of probable composition of the sample is also an important for the analytical procedure. If measuring metals and inorganic anions, cellulose filters should be used while measuring organics, glass-fibre filters should be used. In this thesis work, the sample composition is known and the metals are going to be focused on. For the personal samplers, a filter holder is clipped to the lapel and the pump around the waist. The sampling is usually at a rate of approximately 2 l/min at a 25mm filter. A cyclone can be used to ensure that only the wanted size range of particles can reach the filter. In the cyclone, the gas is spiralled through a conical container in the way that particulate outside the required size range fall into a container at the base of the elutriator, rather than

passing onto the filter. Different from the two methods which using filtration for collection of particulate matters described above, the cascade impactors base on adhesion of particulates on a surface. The particulates are fractionated according to their mass. Air is pumped through the device at a constant rate to impact a number of targets which are coated with petroleum or glycerine jelly. The linear velocity of the air increases by constriction of the flow before each target. If the particle impact above a certain momentum (equals to mass multiply velocity) they would adhere to the targets. Since the air velocity increases through the apparatus successively smaller particles will adhere to each successive surface. The typical operating range is 0.5-200 μm. the operating flow rates can be 1 m^3/h, producing a few micrograms of sample in each fraction per hour of operation when sampling a typical urban atmosphere.

The second step includes sample pre-treatment and preparation although some of the direct sample measurements such as X-ray fluorescence, X-ray emission, neutron activation analysis, and infrared spectrometry have no sample preparation requirement. If the material is readily dissolved, sample dissolution may be used. Due to the solubility of the samples, different solvent are chosen to dissolve the particles. Hydrofluoric acid and nitric acid are commonly used. If the material is difficult to dissolve then the sample dissolution is not required and solid state analytical techniques should be used. The third step is to analyze the prepared samples. When the sample has been dissolved and diluted, the analysis can proceed by numbers of methods for metal ions in solution. For the routine analysis of metals in particulates, atomic absorption spectrometry and visible/ultraviolet absorption spectrometry methods can be used. For less routine analysis and, particularly for the analysis of metals at low concentrations, other technique may be used. Theses include inductively coupled plasma optical emission spectroscopy (ICP-OES), inductively coupled plasma mass spectrometric (ICP-MS), flame atomic emission and atomic fluorescence techniques. (4) The direct solid analysis includes X-ray fluorescence, X-ray emission, neutron activation analysis, infrared spectrometry and so on.

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┌─────────────────────┐
│     Sampling        │──────────────┐        ● High volume samplers
└─────────────────────┘              │        ● Personal samplers
         │
         ▼
┌─────────────────────┐
│      Sample         │
│  pre-treatment and  │──────────────┐        ● Dissolution
│  preparation for the│              │        ● Microwave digestion
│      analysis       │
└─────────────────────┘
         │                                    Techniques requiring treatment:
         ▼                                    ● Atomic absorption spectrometry
┌─────────────────────┐                       ● Visible/ultraviolet absorption
│ Analyze by available│──────────────┐          spectrometry
│      methods        │              │        ● ICP-OES
└─────────────────────┘                       ● ICP-MS
                                              Direct solid analysis:
                                              ● X-ray fluorescence
                                              ● X-ray emission
                                              ● Neutron activation analysis
                                              ● Infrared spectrometry
                                              ● LA-ICP-MS
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Figure 1: The process and techniques of measuring the airborne particles

2.4.1 ICP-MS

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is a very powerful tool for trace (ppb-ppm) and ultra-trace (ppq-ppb) elemental analysis and it is therefore rapidly becoming the technique of choice for trace element analysis in applications ranging from material science to environmental science.

In ICP-MS, a plasma or gas consisting of ions, electrons and neutral particles is formed from Argon gas. The plasma is used to vaporise, atomise and ionise the elements in a sample. The resulting ions are then passed through a series of apertures (cones) into a high vacuum mass analyser. The isotopes of the elements are identified by their mass-to-charge ratio (m/e) and the intensity of a specific peak in the mass spectrum, which is proportional to the amount of that isotope (element) in the original sample, is determined.（7）

Conventionally, particulate samples analyzed by ICP-MS require sample dissolution. Solid samples should be dissolved prior to the analysis, which generally means the whole particles

should be digested in acid so that a liquid can be analysed. It is important to choose the dissolution technique correctly based on the composition of the sample. If the composition of the sample is unknown or the sample contains silicate, hydrofluoric acid which is capable of dissolving silicates may be used. When using this acid, glass apparatus should be avoided and Teflon apparatus is required. If the composition of the particulate sample is known, the dissolution may be less severe depending on the known composition of the sample. The component and digestibility make nitric acid the best choice of acid matrix for ICP-MS analysis typically between 1.5% w/v and 3% w/v. Since ICP-MS is a trace element technique, the quantification range of the ICP-MS is 1000 ppb to 50ppt. (8) Therefore, the more concentrated analytes must be diluted in order to fit into this range. Dilute acid, mild oxidising agent or water may be necessary for dissolution.

To enhance the sample digestion, heating is often necessary. Closed vessel microwave digestion (device is shown in Figure 1) is the most common method at present. Compared with a passive digestion method, hot plate digestion, microwave digestion is welcomed by many benefits such as: keeping the environment in which the reaction takes place clean, closed, and controlled; diminishing the amount of acid to stoichiometric quantities of the reagents, further reducing contamination; ppb, ppt sensitivities; shorter reaction time and improved digestion due to higher temperatures (far above the normal boiling point of the reagents); easy-to-use control software for reproducible results and no loss of volatile elements due to the closed reaction environment. However, the demand of easier, quicker and better techniques is endless, current microwave digestion still suffers from problems: the time (up to hours) of process (acid addition – microwave heating – cooling) and some digestion even requires repetition of the process; waste disposal; the efficiency of the digestion depends on the sample component, the acid, the digestion time and the temperature.

Figure 2: Microwave digestion Device

2.4.2 Laser ablation ICP-MS

Laser ablation inductively coupled plasma mass spectrometry is a technique used for the in situ analysis of trace elements in solid samples. It can determine many elements in the periodic table to high degrees of accuracy and precision. The technique complements electron microprobe analysis, typically measuring trace elements at a lower concentration range (1 ppb - 100 ppm). (9)

For years, though LA-ICP-MS techniques have been no doubt fast developed, their general set-up has not significantly changed as described in **Figure 2**. The sample is placed in an airtight, closed ablation chamber. (1) Solid particles are physically ablated (generating vapor, particles, and agglomerates) due to the interaction of a high power laser beam with the surface of the sample. The particles generated by the laser are carried in a stream of inert gas (helium or argon) into the argon plasma where they are vaporized, atomized and ionized. (9) Subsequently, ions are extracted by the mass analyzer, separated by mass to charge ratio and finally detected. (1) Thus isotopes are measured to determine elemental concentrations. And it is necessary to calibrate signal intensities to determine concentrations.
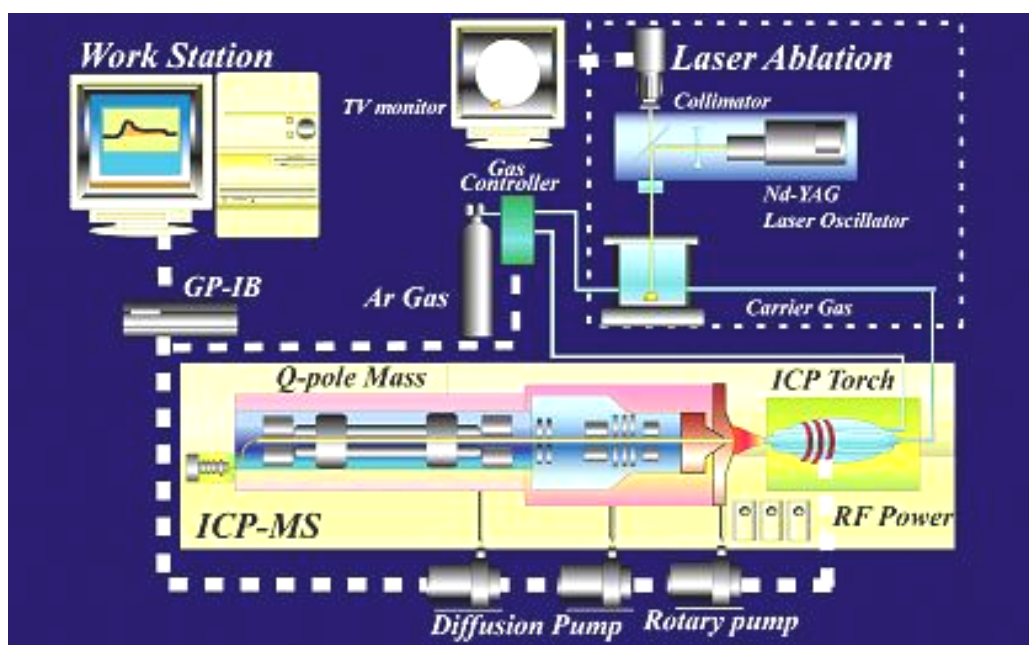
Figure 3: The general set-up of LA-ICP-MS (10)

3. Methodology

3.1 Filter/Sample collection

Airborne particles sampled at two urban sites in Boston (42°22´North; 71°22´West) (the detailed location are shown on the map in **Appendix 1**), Massachusetts from November 2002 to October 2003 were obtained from S. Rauch. (11) There are approx. 600000 people with a total of 3.5 million living in the metropolitan area in Boston. 356000 vehicles were registered in Boston, 2002. (Access report, 5)   Over 375000 vehicles were registered in the City of Boston and another estimated 600000 were driven in daily. (Access report, 5)

Both of the two sampling sites are located in the urban area and have similar PM10 concentrations with an annual arithmetic mean between 20 and 30μg/m^3 for 1989-2001. The two sites are in the proximity of the Massachusetts Turnpike, a major route into Boston with an approximate traffic volume of 120,000 vehicles every day. The first sampling site is located at Kenmore Square at the intersection of 3 high volume roadways; Beacon Street (19000 vehicles per day), Commonwealth Avenue (20000 vehicles per day) and Brookline Street (23000 vehicles per day). The sampler was on a roof of trailer with the inlet at a height of approximately 5 m.(111) The second site is located in Columbus Avenue (10000 vehicles per day), near the intersection with Berkeley Street (20000 vehicles per day), and the sampler was located on the top of a roof at a height of approximately 15m. (11)

Samples were collected for approximately 24 hours starting at 09:00 using a High Volume PM10 impactor (Thermo Anderson, USA) at a flow of approximately 67 m^{3}h^{-1}, resulting in a sample volume of approximately 1500 m^3 per day. The flow rate was continuously monitored and sampling time was recorded. Particles were collected on 20x25 cm cellulose filters (Whatman 41, Whatman, USA). High trace element content in filter materials is a commonly reported limitation in the determination of trace element concentrations in aerosol samples. Whatman 41 filters were selected because of low blank concentrations, although the filters have a slightly, but not significantly, lower retention efficiency under high volume conditions, and their hygroscopic nature does not allow precise weight measurements. (11)

Figure 4: High volume PM-10 Sampler at the Columbus Ave. sampling site.

3.2 Preparation of standards

List of the required material and instrument:
- Whatman filter 41
- ICP-use concentrated multiple metals solution with the concentration of 1000mg/l for each following metals: Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Ti, Zn.
- Colorant: Rhodamine B
- High purity 65% HNO_3
- Milli-Q water
- Pipette and tips
- Oven

Whatman filters were chosen because of the low blank concentrations (10) and keeping the same type as the sampling filters. ICP use solution and nitric acid provide high purity and low interference for the ICP-MS analysis of trace elements. Rhodamine B is chosen because it leaves an obviously visible pink colour on the filter. Furthermore, its molecular formula is $C_{28}H_{31}O_3N_2Cl$ which brings no additional metals into the standard solution. Detailed information of Rhodamine B can be found in **Appendix 2**. Nitric acid is used because most of the metals are soluble with it and it is the typical choice of matrix acid for ICP-MS analysis. The pipette and tips with a minimum volume of 2µl provides a small enough droplet of the

standard solution (**Figure 3**, Spot3-7), although the size of the drop is limited by the minimum of the pipette. The tiny tips help the dropping easily and the spots show small and round on the filter. The dropping method was practiced many times in order to improve the dropping skills and stabilize the shape of the spots. The oven is used for drying the dropped filter in the purpose of stopping the diffusion of the standard solution spots (**Figure 3**, Spot4-7). The standard spots are stable on the filter when they are dry and can be kept for several months.

Comparison of drop size 10µl, 5µl and 2µl; Dried and undried spots; standard with 45.5% HNO_3 and 10.4% HNO_3; Spot1 is 10µl, spot2 is 5µl spot3 and the rest are 2µl drops. Spot1, spot2, spot3 are not immediately dried while Spot4, 5, 6 and 7 are dry immediately after dropping. Spot6 and spot7 are with 45.5% HNO_3 which show a clear edge. Spot7 is the one after laser shooting.

1cm
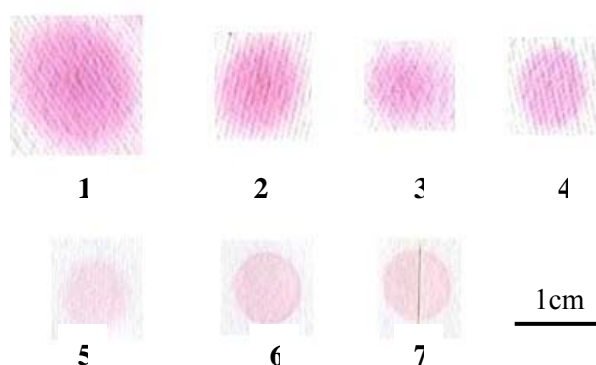
Figure 5: Comparison of drops

Table 1: Comparison of the standard spots dropped in different conditions

	Drop size	Dried	High concentrated HNO_3	Clear edge
Spot1	10µl	X	X	X
Spot2	5µl	X	X	X
Spot3	2µl	X	X	X
Spot4	2µl		X	X
Spot5	2µl		X	X
Spot6	2µl			
Spot7	2µl			

To check the precision of the dropped spots size the average radius of spots (2μl) are list below:

Table 2: the radius of the spots (2μl)

	r(mm)
Spot1	3.79
Spot2	3.59
Spot3	3.71
Spot4	3.80
Spot5	3.63
Spot6	3.56
Spot7	3.90
Spot8	3.73
Spot9	3.79
Spot10	3.75
Spot11	3.73
Spot12	3.51
Spot13	3.75
Spot14	3.64
Spot15	3.71
Spot16	3.64
Spot17	3.73
Spot18	3.65
Average	3.70
STDEV	0.09

The preparation procedure:

In terms of various concentrations, the standards are labelled A, B, C, D, E, F. The concentrations of the standards were prepared at 0ppm, 1ppm, 10ppm, 20ppm, 50ppm, 100ppm to obtain an accurate slope for calibration. Several colorants (Rhodamine B, $KMnO_4$, I, etc.) were tested and Rhodamine B was finally chosen for its heavy pink/violet colour and dyeing efficiency. However, during the experiment, it was found that Rhodamine B may react with some of the heavy metals in the water and form a precipitation in the solution. This problem can be solved by adding much more nitric acid. When much nitric acid contained in the solution, the precipitation would not be formed. But Ag remains difficult to keep stable with Rhodamine B in the nitric acid in the nitric acid solution. This may be due to the chemical component of Rhodamine B that contains a "Cl" which may react with Ag^+ to form a compound that has little solubility. As well as the reason described above, the standard solution contains as high as approximately 45.5% HNO_3 can help the drop of standard leave a very clear edge around the spots on the filter (like spot 6 and 7 in the Figure 3). Therefore, it is very convenient to find the edge of the pink spots under the microscope during the LA ICP-MS analysis so that the size of the spots (diameter) can be measured more accurate. The

amount of chemicals used in the preparation of the standard is shown in Table 3.

Table 3: The concentration of the chemicals in the standard solution

STANDARD nO.	A	B	C	D	E	F
Concentration of the metals (ppm)	0	1	10	20	50	100
Colorant (g/l)	0.25	0.25	0.25	0.25	0.25	0.25
65% HNO_3 l/l	0.7	0.7	0.7	0.7	0.7	0.7

The detailed preparation procedure is described as follows:

Firstly, add 0.125g Rhodamine B flaky crystal into 100ml Milli-Q water to make a 1.25g/l dye solution. Using a plastic or glass stick to mix round and avoiding the metal ones so that the dye would not contaminated by the metal mixer. Secondly, to make a volume of 10ml standard solution for each concentration, 0μl, 10μl, 100μl, 200μl, 500μl, 1000μl 1000mg/l concentrated ICP standard solution are added into the 10ml volumetric flask. Then add 7ml 65% HNO_3 into each volumetric flask. After that, add 2ml prepared dye solution into each flask. At last, fill the volumetric flask up to 10ml with Milli-Q water. Shake slightly to mix the liquid well. Thirdly, place a piece of Whatman filter on a clean plate; make sure the back side of the filter does not touch the plate. This is in the purpose of avoiding any lose of the standard drops so that the volume of the standard solution added on the filter can be more accurate. Then pipette out 2μl standard solution from the volumetric flask and drop it on the filter. A pink spot at a size of approximately 7mm in diameter is made on the filter. Repeat the dropping for each prepared standard solutions. Lastly, put the dropped filter into the oven immediately at a temperature over 120°C for about 2-3 minutes to dry. Finally when the standards are ready prepared, keep them in a dry and clean environment until analysis.

3.3 Analysis

3.3.1 Testing and choosing Laser operating conditions

The standard solutions were prepared at various concentrations: 0ppb, 1ppb, 10ppb, 100ppb, 1ppm, 10ppm, 20ppm, 50ppm, 100ppm. Amount which 1ppb and 10ppb are too low to be detected on the filter by LA ICP-MS. Thus 0ppm, 1ppm, 10ppm, 20ppm, 50ppm, 100ppm were finally chosen as the suitable standard for calibration.

In order to select the suitable operating conditions of LA ICP-MS analysis, standard D (20ppm) was tested as a sample. The laser beam should be strong enough to shoot through the filter in order to carry all the stuff into the ICP-MS at the shot area. But it is not necessary to be too powerful to destroy the base under the filter. The laser beam spots sizes 1, 2, 4, 5, 6, 7; energies at 5, 10, 15, 20; repetition rates at 10Hz, 20Hz and speeds at 10μm/s, 50μm/s,

100μm/s and 200μm/s were tested. **Figure 4** below shows the relation between the laser spots size, energy and speed and the intensity of the standard sample measured by ICP-MS. It mainly figures out the reason of selecting the operating conditions. Pb values are taken as an example.
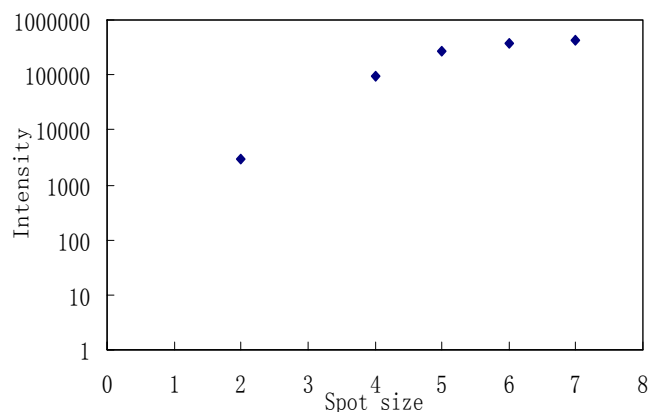
The left figure shows the relation between the laser spots size and the intensity of the standard sample measured by ICP-MS. It can be found that the intensity changes little when the laser spots size reaches 7. (The energy is set to 15, repetition is set to 20Hz and the speed is 100μm/s)
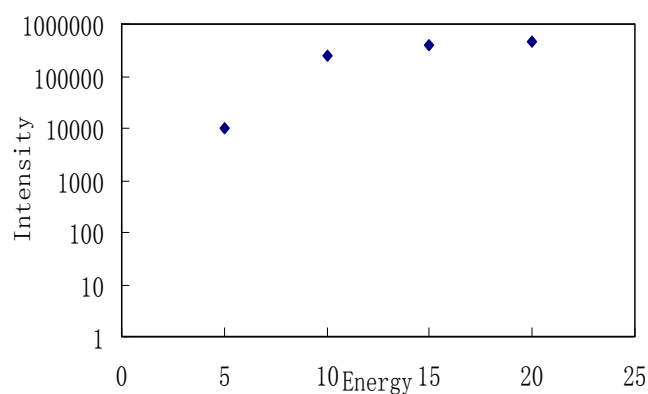
The left figure shows the relation between the laser energy and the intensity of the standard sample measured by ICP-MS. The intensity tends to be stable when the laser energy reaches around 15. (The laser spot size is 7, repetition rate is 20Hz and laser speed is 100μm/s)
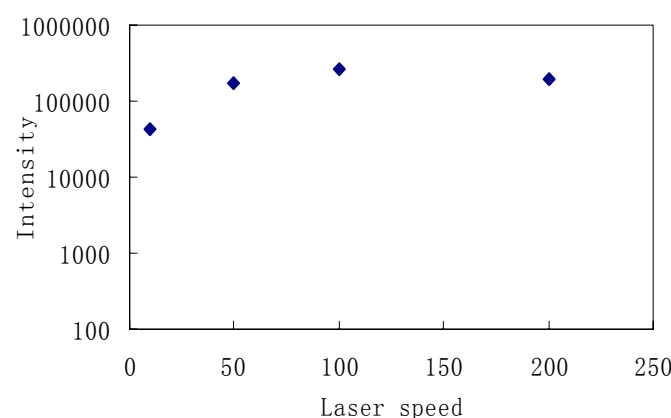
The left figure shows the relation between the laser speed and the intensity of the standard sample measured by ICP-MS. The intensity tends to be stable when the laser speed reaches around 100μm/s. (The laser spot size is 7, repetition rate is 20Hz and energy is 10)

Figure 6: The relationship between laser spots size, energy and speed and the intensity measured by ICP-MS

To sum up, energy at 15 (2.2mj), laser beam size 7, repetition rate at 20Hz and the laser speed

of 100μm/s were chosen as the suitable operation condition at last.

Typical operating parameters for LA ICP-MS are summarized in **Table 4**.

Table 4: LA ICP-MS Operating Conditions

ICP-Ms	
rf power	1200 j
Plasma Ar gas flow rate	16 l/min
Auxiliary Ar gas flow rate	0.9 l/min
Nebulizer Ar gas flow rate	1 l/min
Scanning mode	Peak hopping
Dwell time	20s
Time per sweeps	3.105s
Reading per replicate	10
Laser system	
Energy	15 (2.2mj)
Size of laser beam	7 (300μm)
Repetition rate	20Hz
Scanning speed	100μm/s

The airborne sample labelled Kenmore1.2, Kenmore 1.5, Kenmore 2.2, Kenmore 2.6, Columbus1.5, Columbus 1.8, Columbus 2.1, Columbus 2.2 were analyzed as well as the blank filter, standard A, B, C, D, E and F. Intensities of Al27, Cr52, Cr53, Mn55, Fe57, Co59, Ni58, Cu63, Zn64, Ag107, Cd114, Ba138 and Pb208 were monitored to determine the concentration of these elements.

4. Results and discussion

In principle, with knowing of the following parameters, the concentration of the metals in the air can be calculated:

- The total sample volume
- The area of the sampling filter
- The concentration of the standard solution
- The volume of the drop
- The area of the spot
- The metals intensity on the sampling filter
- The metals intensity on the blank filter
- The metals intensity on the standard spots

So the concentration of the metals in the air can be calculated by equation (i).

$$C = \frac{D \times A}{V} \qquad \text{(i)}$$

Where: C means the concentration of the metals in the air;
D means the density of the sample on the filter after the calibration;
A means the area of the sampling filter;
V means the total volume of the sampling air.

During the analysis, several standard spots with the known elemental concentrations are analyzed at the same time with the samples. According to the known concentrations and the analyzed intensity values, a slope can be gained to calibrate the accurate intensity of the samples on the filters.

4.1 Analysis of standard and samples

With the known concentration and drop size of each standard. The theoretical density on the spots can be easily calculated by:

$$D = \frac{C \times V}{A} \qquad \text{(ii)}$$

Where: D is the theoretical density on the spot;
C is the concentration of the standard;
V is the volume of the drop;
A is area of the spot.

During the analysis, both vertical and horizontal diameters of each spot were measured. Since the spot can be considered as round circle, the area of each spot is calculated by πr^2 using the average diameter. In this experiment, the volume of the drop is 2 μl and the concentrations of the standards are 0ppm, 1ppm, 10ppm, 20ppm, 50ppm, 100ppm. Three group of standard were made for three calibrations. The diameter (d1 and d2 are vertical and horizontal diameters, d is the average of d1 and d2), the radius (r), the area (A), the concentration of the standard drops (C) and the theoretical density of the standard spots (density) are presented in **Table 5**.

Table 5: The diameter, area and theoretical density of the standard spots

(a) Spot size and theoretical density of the standard spots of Calibration 1:

	A(0ppm)	B(1ppm)	C(10ppm)	D(20ppm)	E(50ppm)	F(100ppm)
d1(mm)	7.72	7.05	7.55	7.47	7.15	7.05
d2(mm)	7.43	7.3	7.3	7.72	7.36	7.17
d(mm)	7.575	7.175	7.425	7.595	7.255	7.11
r(mm)	3.788	3.588	3.713	3.798	3.628	3.555
A(mm2)	45.07	40.43	43.30	45.31	41.34	39.70
C(g/m3)	0	1	10	20	50	100
Density(g/m2)	0	4.94647E-05	4.62E-04	8.83E-04	2.42E-03	5.04E-03

(b) Spot size and theoretical density of the standard spots of Calibration 2:

	A(0ppm)	B(1ppm)	C(10ppm)	D(20ppm)	E(50ppm)	F(100ppm)
d1(mm)	7.9	7.62	7.42	7.21	7.74	6.67
d2(mm)	7.68	7.3	7.74	7.8	7.18	7.36
d(mm)	7.79	7.46	7.58	7.505	7.46	7.015
r(mm)	3.895	3.73	3.79	3.7525	3.73	3.5075
A(mm2)	47.66	43.71	45.13	44.24	43.71	38.65
C(g/m3)	0	1	10	20	50	100
Density(g/m2)	0	4.58E-05	4.43E-04	9.04E-04	2.29E-03	5.17E-03

(c) Spot size and theoretical density of the standard spots of Calibration 3:

	A(0ppm)	B(1ppm)	C(10ppm)	D(20ppm)	E(50ppm)	F(100ppm)
d1(mm)	7.49	7.49	7.8	7.24	6.95	7.67
d2(mm)	7.49	7.05	7.05	7.3	7.95	6.92
d(mm)	7.49	7.27	7.425	7.27	7.45	7.295
r(mm)	3.745	3.635	3.713	3.635	3.725	3.6475
A(mm2)	44.06	41.51	43.30	41.51	43.59	41.80
C(g/m3)	0	1	10	20	50	100
Density(g/m2)	0	4.82E-05	4.62E-04	9.64E-04	2.29E-03	47.85E-03

*The volume of each drop is 2μl.

While the laser is firing the standard or samples, element signals are obtained from the ICP-MS. The following 2 figures show the ICP-MS response/intensity associated with time. A 100ppm standard and a sample filter are chosen for example (**Figure 5 and 6**). The peak appears when the laser starts ablating the standard/sample. The standard values (intensity) are obtained by averaging each of the peaks formed by ablating each standard spot. The sample values are obtained by average the peaks of the samples. Therefore both the standard and samples values (intensity) are obtained. **Table 6** shows the ICP-MS response/intensity of all standard (subtracted by 0ppm standard) and samples (subtracted by blank filter).
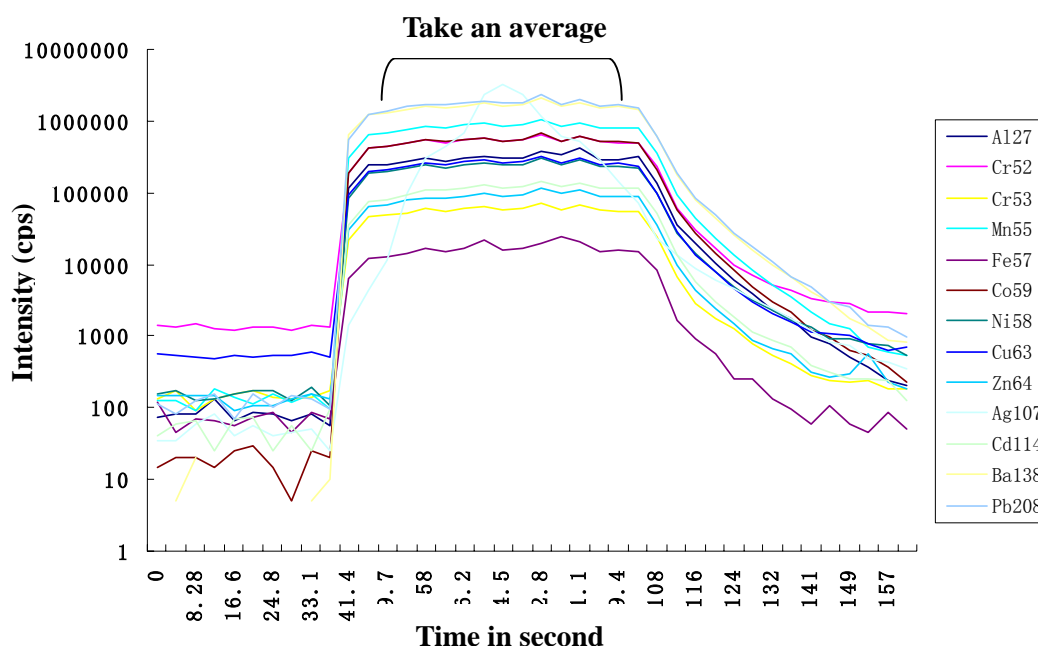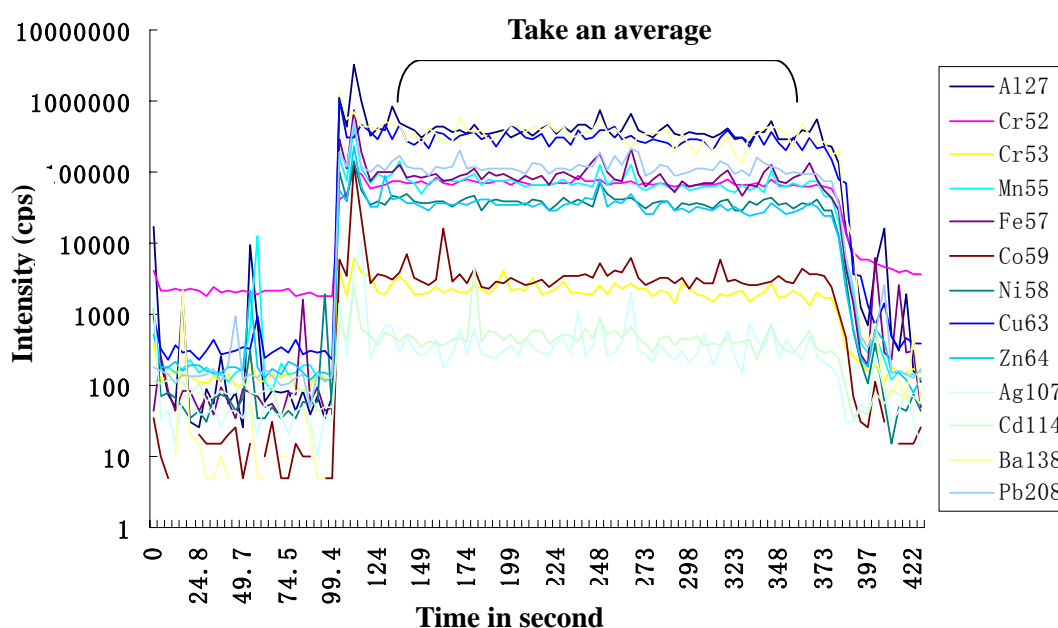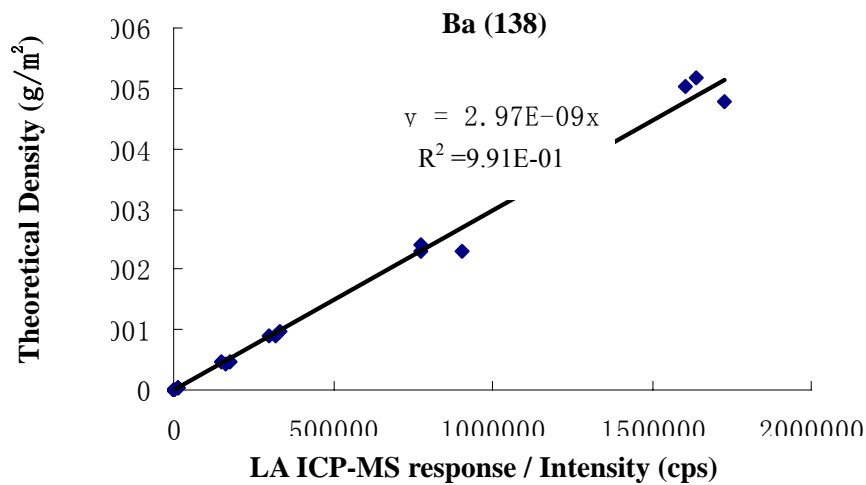

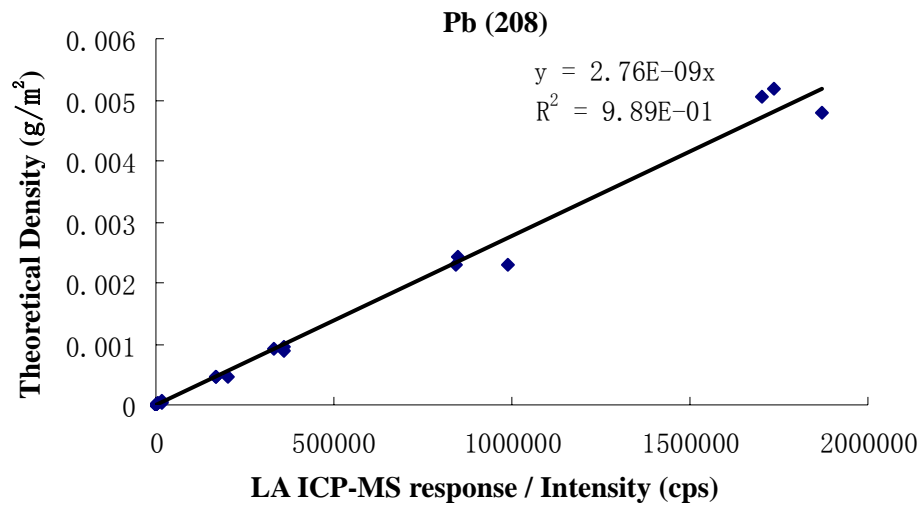*Figure 7: ICP-MS signal of the standard (100ppm)*

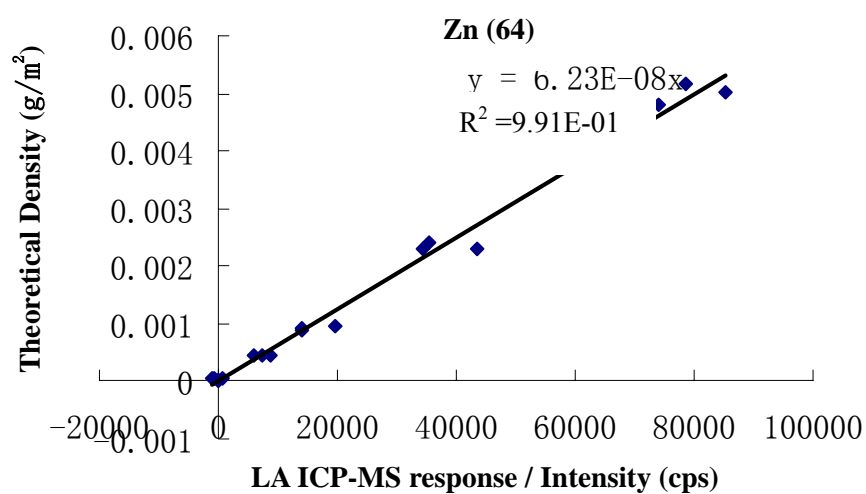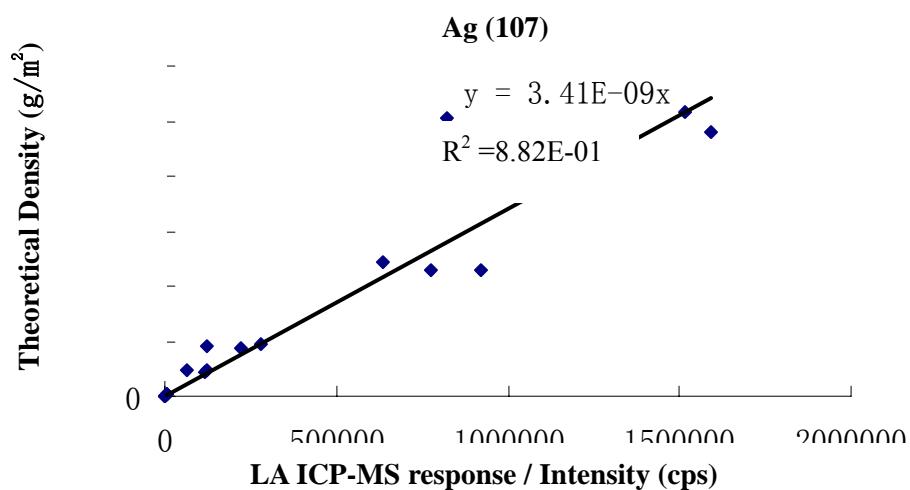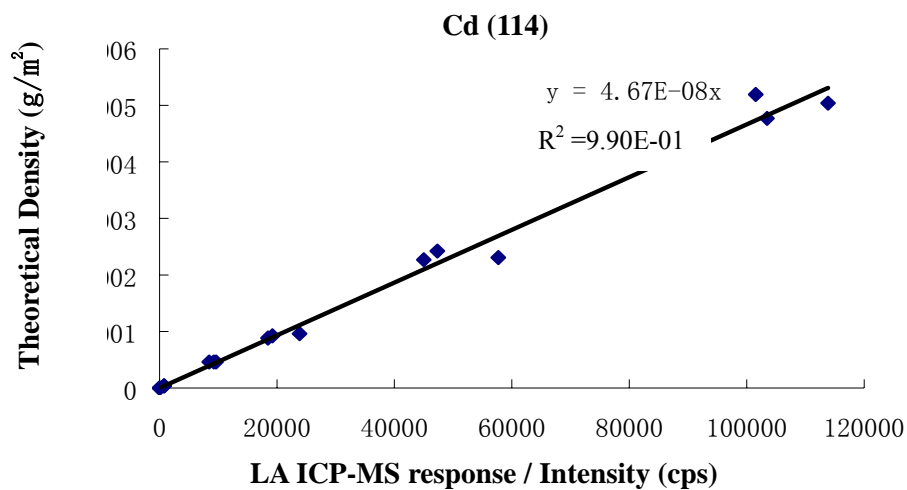*Figure 8: ICP-MS signal of the Sample*

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Table 6: ICP-MS response/intensity (average values) of all standard (subtracted by 0ppm standard) and samples (subtracted by blank filter)
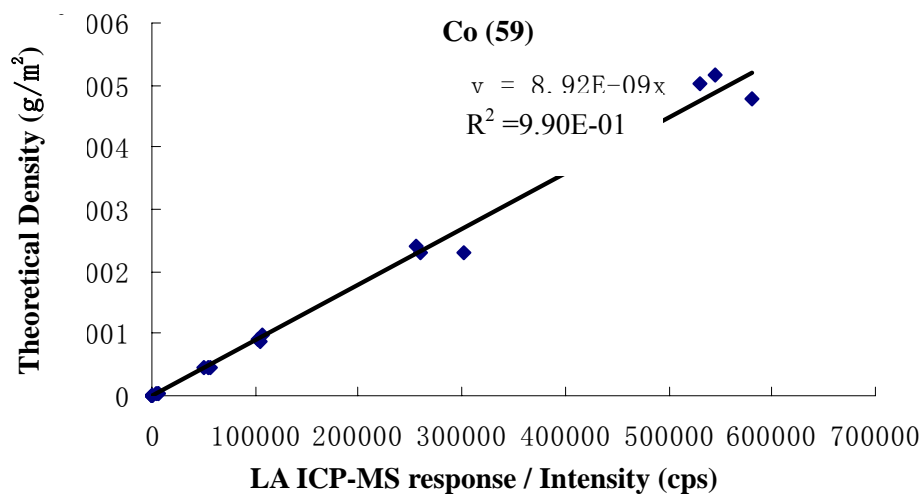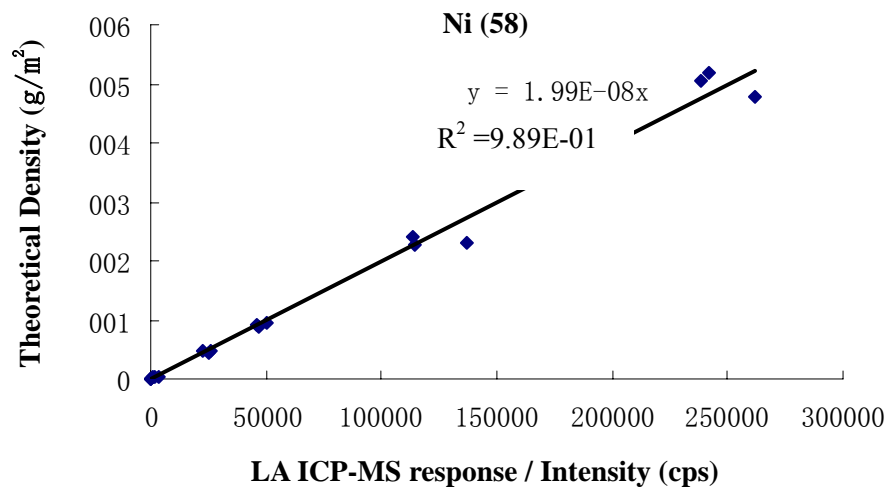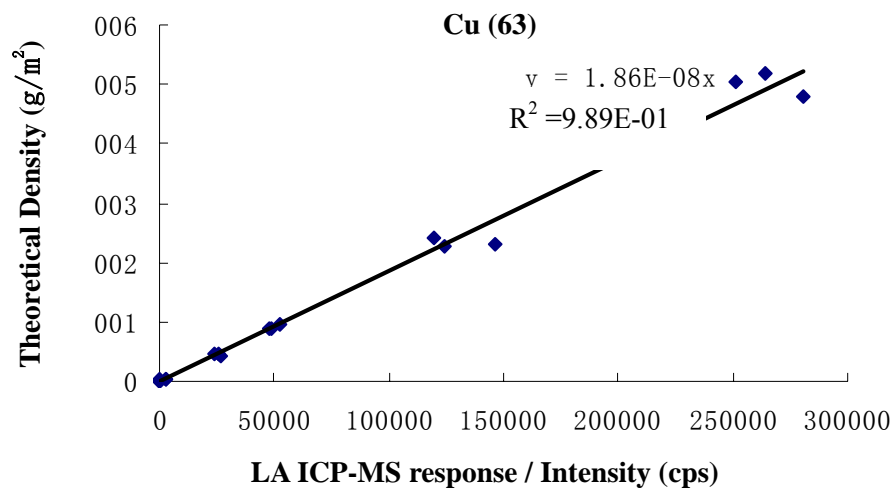
			Al27	Cr52	Cr53	Mn55	Fe57	Co59	Ni58	Cu63	Zn64	Ag107	Cd114	Ba138	Pb208
Standard	Calibration1	0ppm	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		1ppm	-35632.9	6614.5	472.5	9182.9	-3009.3	4448.1	907.4	57.3	-1005.2	4794.6	815.9	14565.2	16579.4
		10ppm	40622.0	53046.0	5984.2	88015.1	6269.1	56536.5	26306.0	25509.4	8889.4	119660.2	9659.1	175962.1	201120.5
		20ppm	45252.2	97075.7	11141.0	164218.9	250.1	104820.7	47044.0	47965.9	14089.8	224432.1	18453.0	322339.8	358510.1
		50ppm	108987.6	231577.7	27204.8	401020.6	6094.8	255160.8	113248.6	119952.1	35431.8	637696.8	47412.4	777254.8	847844.0
		100ppm	253600.9	476302.4	57063.0	833654.1	12389.7	529714.4	238013.8	251393.5	85433.0	821723.1	113903.1	1602204.4	1704940.5
	Calibration2	0ppm	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		1ppm	-5038.2	5338.3	588.4	7731.1	-581.3	5511.2	2009.4	2503.5	-644.8	5943.0	852.7	13264.5	7095.1
		10ppm	41888.9	45940.2	5717.7	90192.1	4865.9	54922.5	25143.7	26361.6	7477.3	117587.3	8562.0	161349.3	169741.5
		20ppm	12856.4	80548.9	10625.5	159119.1	2540.6	102544.7	45566.8	49067.1	14180.3	121637.8	19411.2	299685.9	330908.0
		50ppm	88900.1	222655.7	27794.0	406151.5	4631.1	260331.1	114749.3	124429.3	34262.0	921634.6	44869.4	772671.7	845488.7
		100ppm	276249.2	481793.5	59019.6	858914.2	13528.1	544405.4	242071.6	263680.7	78752.0	1517933.0	101357.2	1638838.8	1736745.4
	Calibration3	0ppm	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		1ppm	3285.5	3003.9	560.0	11943.0	-445.6	5596.9	3392.7	3113.6	541.4	5575.5	955.4	15863.0	18412.2
		10ppm	12015.1	42536.4	5220.0	78739.4	160.3	50414.7	22775.5	23894.5	5995.3	66893.5	9063.1	148975.5	166014.2
		20ppm	71361.5	93813.8	11500.8	170521.9	4387.2	107841.6	50265.8	52493.2	19621.1	278276.3	23946.2	333729.7	360982.5
		50ppm	148562.4	265523.5	32510.8	477582.0	7671.0	302276.4	136748.1	146004.7	43348.1	777803.8	57523.4	906839.2	986746.0
		100ppm	312952.2	519922.0	63689.1	925336.6	15671.7	581016.7	261585.2	280703.2	74123.0	1593696.9	103648.9	1730600.3	1873111.9
Samples		K1.2	195773.4	1764.8	734.6	31681.9	32466.9	2638.7	15070.7	95220.0	17857.4	648.1	557.4	97412.2	71747.2
		K1.5	357252.9	16764.8	1465.6	67825.6	84938.2	3211.8	37304.5	307783.9	33370.5	259.3	432.9	348897.1	117036.8
		K2.2	327418.0	7467.1	1080.9	44410.3	59992.4	1768.0	18431.1	126510.7	16861.2	72.4	606.2	194099.9	73434.4
		K2.6	362392.6	11840.6	1949.8	71743.8	76967.9	2823.0	37383.0	109835.4	24667.5	324.3	775.0	275310.0	103289.5
		CD1.5	377439.0	12576.3	1235.8	60353.3	58630.0	5375.2	17506.7	74206.8	31255.2	949.7	439.4	100961.6	66103.2
		CD1.8	293536.1	5557.3	847.1	33013.9	40001.0	1926.9	12854.7	34635.3	12882.8	186.0	241.2	105942.7	51411.7
		CD2.1	451637.5	-67.1	788.9	46953.4	50755.9	1936.7	13348.2	94024.3	14528.7	203.6	194.5	143627.4	61675.4
		CD2.2	466589.1	3271.8	939.3	46004.3	57566.8	2961.3	12332.6	45785.6	13795.6	481.5	277.3	151311.1	63799.3

4.2 Calibration

Using the calculated Theoretical density (g/m^2) and the LA ICP-MS response/intensity (cps), calibration curve for each measured element are obtained. They are shown in the **Figure 7**. Three calibration data are put together in a single figure. Each calibration curve is obtained from all three calibration data.

Cd (114)

Theoretical Density (g/m^2)

y = 4.67E−08x

R^2 =9.90E-01

LA ICP-MS response / Intensity (cps)

Ag (107)

Theoretical Density (g/m^2)

y = 3.41E−09x

R^2 =8.82E-01

LA ICP-MS response / Intensity (cps)

Zn (64)

Theoretical Density (g/m^2)

y = 6.23E−08x

R^2 =9.91E-01

LA ICP-MS response / Intensity (cps)

Cu (63)

Theoretical Density (g/㎡)

v = 1.86E-08x

R^2 =9.89E-01

LA ICP-MS response / Intensity (cps)

Ni (58)

Theoretical Density (g/㎡)

y = 1.99E-08x

R^2 =9.89E-01

LA ICP-MS response / Intensity (cps)

Co (59)

Theoretical Density (g/㎡)

v = 8.92E-09x

R^2 =9.90E-01

LA ICP-MS response / Intensity (cps)

Fe (57)

y = 3.28E-07x

R^2 =8.49E-01

Mn (55)

y = 5.65E-09x

R^2 =9.89E-01

Cr (53)

v = 8.24E-08x

R^2 =9.89E-01

Figure 9: The Calibration Curves for the elements: Al27, Cr52, Cr53, Mn55, Fe57, Co59,
Ni58, Cu63, Zn64, Ag107, Cd114, Ba138 and Pb208.

During the calculation, the LA ICP-MS response/intensity (cps) background is removed by subtracting from the values of 0ppm standard. Therefore the curves must go through the zero point. Thus the curve can be expressed as:

$$Y = A*X \qquad\qquad \textbf{(iii)}$$

A is coefficient;
Y is theoretical density (g/m^2) calculated by equation (ii);
X is the LA ICP-MS response/intensity (cps) of the standard.

The value of A for the measured elements is shown in the **Table 7**:

Table 7: The calibration slope A, correlation coefficient R^2 and analytical performance

Elements	A	R^2	Detection Limit	Sensitivity (cps/(g/m^2))
Al27	1.76E-08	0.945	94.8	5.70E+07
Cr52	1.0E-08	0.99	0.489	9.97E+07
Cr53	8.24E-08	0.989	1.671	1.21E+07
Mn55	5.65E-09	0.989	4.938	1.77E+08
Fe57	3.28E-07	0.849	294.3	3.05E+06
Co59	8.92E-09	0.99	0.6498	1.12E+08
Ni58	1.99E-08	0.989	8.28	5.02E+07
Cu63	1.86E-08	0.989	48.83	5.38E+07
Zn64	6.23E-08	0.991	30.68	1.61E+07
Ag107	3.41E-09	0.882	0.061	2.93E+08
Cd114	4.67E-08	0.99	0.7185	2.14E+07
Ba138	2.97E-09	0.991	7.988	3.37E+08
Pb208	2.76E-09	0.989	5.471	3.62E+08

Using equation (iii), the calibrated density on the sample filters can be gained by:

$$I = A*I' \tag{iv}$$

I is the calibrated density (g/m^2) on the sample filters;
A is the coefficient the same as the equation (iii) gained from the calibration curves;
I' is the LA ICP-MS response/intensity (cps) of the sample.

Substitute I into equation (i), the concentrations of metals in the air are obtained. The results of measured elements are in the **Table 8.**

Table 8: The results of concentration (ng/m3) of metals in the air

	Al (based on Al27)	Cr (based on Cr52)	Cr (based on Cr53)	Mn (based on Mn55)	Fe (based on Fe57)	Co (based on Co59)	Ni (based on Ni58)	Cu (based on Cu63)	Zn (based on Zn64)	Ag (based on Ag107)	Cd (based on Cd114)	Ba (based on Ba138)	Pb (based on Pb208)
K1.2	94.8	0.489	1.671	4.938	294.3	0.6498	8.280	48.83	30.68	0.0610	0.7185	7.988	5.471
K1.5	173.1	4.641	3.334	10.570	769.8	0.7910	20.496	157.84	57.34	0.0244	0.5581	28.611	8.925
K2.2	158.6	2.067	2.459	6.921	543.7	0.4354	10.127	64.88	28.97	0.0068	0.7814	15.917	5.600
K2.6	175.6	3.278	4.435	11.181	697.6	0.6952	20.539	56.33	42.39	0.0305	0.9990	22.577	7.877
CD1.5	182.9	3.481	2.811	9.406	531.4	1.3237	9.619	38.05	53.71	0.0894	0.5664	8.279	5.041
CD1.8	142.2	1.538	1.927	5.145	362.5	0.4745	7.063	17.76	22.14	0.0175	0.3110	8.688	3.921
CD2.1	218.8	0	1.795	7.318	460.0	0.4770	7.334	48.22	24.96	0.0192	0.2507	11.778	4.703
CD2.2	226.0	0.906	2.137	7.170	521.7	0.7293	6.776	23.48	23.71	0.0453	0.3574	12.408	4.865
Average	171.5	2.048	2.571	7.831	522.6	0.6970	11.279	56.92	35.49	0.0368	0.5678	14.531	5.800
Std.Dev.	41.9	1.628	0.937	2.340	157.6	0.2857	5.824	43.75	13.89	0.0273	0.2578	7.493	1.708
Detection limit	19.7	2.94	0.54	1.25	102	0.15	1.26	2.45	4.23	0.04	0.09	0.15	0.4

*   K1.2 -- Kenmore 1.2
       K1.5 -- Kenmore 1.5
       K2.2 -- Kenmore 2.2
       K2.6 -- Kenmore 2.6
       CD1.5 – Columbus 1.5
       CD1.8 – Columbus 1.8
       CD2.1 – Columbus 2.1
       CD2.2 – Columbus 2.2

4.3 Analysis of airborne particles (quality control)

4.3.1 Comparison with previous data

Among the measured elements Al27, Cr52, Cr53, Mn55, Fe57, Co59, Ni58, Cu63, Zn64, Ag107, Cd114, Ba138 and Pb208, only Cu, Pb, Zn, Cd were analysed previously by ICP-MS after sample digestion (microwave assisted digestion in concentrated acids). The current and previous values for these elements are compared in **Table 9**.

Table 9: Previous data obtained by conventional ICP-MS analysis after sample digestion

Variable		Valid N	Mean	Confidence-95%	Confidence+95%	Min.	Max.	Std.Dev.
Cu	Pre.	12	56.07824	47.95081	64.2057	37.72255	72.2041	12.79165
	New	8	56.92375	20.34914	93.4984	17.76	157.84	43.74849
Pb	Pre.	12	7.23999	5.78024	8.6997	3.79580	11.2617	2.29748
	New	8	5.80038	4.37276	7.22799	3.921	8.925	1.70764
Zn	Pre.	12	32.14368	22.69066	41.5967	17.22363	67.8411	14.87798
	New	8	35.4875	23.8752	47.0998	22.14	57.34	13.88997
Cd	Pre.	12	0.24214	0.18210	0.3022	0.12959	0.4855	0.9449
	New	8	0.56781	0.35231	0.78332	0.2507	0.999	0.25777

The caption "Descriptive Statistics" spans the columns Valid N, Mean, Confidence-95%, Confidence+95%, Min., Max., Std.Dev.

The current results of Pb and Cd show better because of the lower standard deviation. The current mean value of Cu is very close to the previous value. However its standard deviation is high. Zn seems as good as the precious data and with lower standard deviation. Although current value of Cd has a better standard deviation, its mean value is over twice of the previous data. The difference may due to various analytical conditions such as time, the numbers of samples, the measure and analytical techniques and interferences.

4.3.2 Interference

As a sensitive technique for analysing trace and ultra-trace elements, ICP-MS has relatively large problems with interferences. E. Hywel Evans subdivided the interference encountered in ICP-MS into two categories: Spectroscopic Interferences and Non-spectroscopic Interferences. (12) Spectroscopic interferences are caused by atomic or molecular ions having the same nominal mass as the analyte of interest, therefore interfering with the analysis by causing an erroneously large signal at the m/z of interest. There is one type of spectroscopic interferences that caused by overlapping isotopes of different elements. These interferences are easy to predict and well documented, so they can be easily overcome by utilizing alternative isotopes or elemental equations for analysis. (12) For example, if measuring Cr50, there are Ti50 and V50 interferences. But Cr53 or Cr52 do not have this problem. Measuring Zn64 as another example, there is Ni64 interference, but the ratio is known and automatically calculated in the ICP-MS software. Another type of the spectroscopic interferences is that of molecular or polyatomic-ion interferences caused by polyatomic ions formed from precursors in the plasma gas, entrained atmospheric gases, water, acids used for dissolution and sample matrix. The polyatomic ions so formed, may then result in interferences on analytes with the same

nominal m/z. (12) In the case of this work, the interferences caused by polyatomic ions formed from water, acid used for dissolution and to some extent sample matrix can be ignored. Because the samples are detected directly by LA ICP-MS without any water, dissolution acid and limited sample matrix. Oxides for instance are known to be greatly reduced in LA-ICP-MS. Unlike the spectroscopic interferences, the non-spectroscopic interferences is characterized by a reduction or enhancement in analyte signal due to factors exerting an influence on sample transport, ionisation in the plasma, ion extraction, or ion throughput in the resultant ion beam. (12) In this part, the experiments are focused on the analysis of spectroscopic interferences caused by molecular and polyatomic ion with the same nominal m/z as analytes. The "ELEMENT 2 ICP-MS" software was used to determine the possible basic interferences of the analyte metals are list in the Appendix 3. Furthermore, based on the natural existing possibilities, the most likely interfering molecules and double charged ions are selected for interference analysis. (**Table 10**)

Table 10: The most probable interferences

	Basic interference
Al27	53Cr++, 54Cr++, 54Fe++, 55Mn++
Cr52	12C40Ar
Cr53	106Cd++, 13C40Ar, 107Ag++
Mn55	15N40Ar, 111Cd++
Fe57	114Sn++, 114Cd++, 115Sn++
Co59	117Sn++, 118Sn++, 23Na36Ar, 119Sn++
Ni58	115Sn++, Fe, 116Sn++, 116Cd++, 117Sn++
Cu63	25Mg38Ar, 27Al36Ar, 23Na40Ar, 117Sn++
Zn64	127I++, Ni, 28Si36Ar, 26Mg38Ar, 24Mg40Ar
Ag107	67Zn40Ar
Cd114	76Se38Ar, 74Ge40Ar, 76Ge38Ar, 78Se36Ar, 74Se40Ar, Sn
Ba138	Ge, La
Pb208	

Additionally, if the concentration of analytes in the sample is very large (e.g. 100ppm) while the interferences are very small (e.g. 0.1ppm), the interferences can be ignored. It is possible to check for possible interferences in synthetic solution by measuring the element of interest in a solution containing only the interfering element. For instance, to check for the interference of 25Mg38Ar on the analysis of Cu63 for example, one can analyse Cu a solution containing Mg only; if no Cu detected in the Mg solution, there is no problem with this interference. If Cu is detected in the Mg solution, the ratio of Cu63/Mg25 can be calculated and this ratio can be used for correction.

Solutions (100ppm) with single element (Fe, Se, Ag, I, Si, Sn, Mn, Cr, Ni, Cd, Zn, Mg) were prepared and dropped on the blank filter to analyze the possible interferences. The isotopes Al27, Cr52, Cr53, Mn55, Fe57, Co59, Ni58, Cu63, Zn64, Ag107, Cd114, Ba138, Pb208, I127, Na23, Mg24, Si28, Sn115, Sn117, Cd111, Zn67, Fe54, Se74, Cd106, Cd116 and Mg25 are measured in the experiment. The results are shown in **Table 11.** The first row is the various

standards while the first column is the elements detected. The values are the ICP-MS response/intensity from which blank values were subtracted. The first column of value (Fe column) where Fe54 was suspected to interfere Al27 shows no problem with the interference owing to the negative value. The columns Se, Mn, Cr and Mg have the same negative value as Fe column so that in this experiment, there are no problem with Se74, Se76 and Se78 interfere Cd114; no problem with Mn55 interfere Al27; no problem with Cr53 and Cr54 interfere Al27, and no problem with Mg25 interfere Cu63 and Mg26 interfere Zn64. In the third column (Ag column), there is a signal of Cr53 detected at a value of 58.8, that means while there is a Ag107 (intensity is 2104344.3) contained in the analyte, 0.0028% (58.8/2104344.3) of the Ag107 intensity in the sample may become the interference of Cr53. However, in this case, the ratio 0.0028% is so small that can be ignored. In I column, Zn64 is detected at the intensity value of 2965.4 while I127 are 34768.6, the ratio Zn64/I127 is 0.08529. In Si column, there is an intensity of 5270.5 Zn64 detected while 4179945.8 Si28 detected. The ratio of Zn64/Si28 is 0.01261. In Sn column, the intensity of 22093.7 Fe57, the intensity of 2710.4 Ni58 and the intensity of 87 Co59 are detected while the intensity of 9165 Sn115 and 119421.8 Sn117 are detected. So the ratio of Fe57/Sn115 is 2.41, the ratio of Ni58/Sn115 is 0.2957 and the ratio of Co59/Sn117 is 0.000729. In Cd column, the intensity of Cr53, Mn55 and Fe57 are negative which show no problem with Cd106 interfere Cr53, Cd111 interfere Mn55 and Cd114 interfere Fe57. But an intensity of 515.2 Ni58 is detected and Cd116 intensity is 44364.7. So the ratio of Ni58/Cd116 is 0.01161. In Zn column, the intensity of 180.4 Ag107 is detected and 18931 Zn67 is detected. The ratio of Ag107/Zn67 is 0.00953. The ratio of Cr53/Ag107, Zn64/I127, Fe57/Sn115, Ni58/Sn, Co59/Sn117, Ni58/Cd116 and Ag107/Zn67 are shown in the **Table 12**.

The ICP-MS response/intensity (subtracted by the blank filter) of the six samples is shown in the **Table 13.**
Table 13

Table 11: Interferences detection results by LA-ICP-MS

	Fe	Se	Ag	I	Si	Sn	Mn	Cr	Ni	Cd	Zn	Mg
Al27	-81890.9	206729.3	-22665.3	-67433.4	155917.8	227770.4	-91640.2	-122782.2	-97721.8	-79569.9	-127374.0	-150361.2
Cr52	2032.2	3668.5	-182.1	1393.7	421.7	-3996.0	-5316.2	575725.5	-3645.5	-1729.8	1908.5	13412.4
Cr53	-28.9	188.8	58.8	-38.0	124.1	250.6	-64.4	70342.2	43.4	-18.1	11.2	-62.2
Mn55	-1115.3	12636.3	961.5	2095.4	30897.9	66237.1	1146970.7	-4661.0	5668.8	-4194.5	-5210.4	-2641.0
Fe57	15818.6	10892.5	4427.5	1820.0	16530.7	22093.7	3710.9	-3288.8	-98.5	-121.0	-3262.4	-685.5
Co59	-2212.3	-1846.4	-1180.0	-741.5	-169.1	87.1	-2128.9	-2163.3	-2023.6	-1324.4	-2253.0	-2314.7
Ni58	2184.4	1340.1	171.9	-108.4	4285.5	2710.4	-310.0	367.3	277464.2	515.2	-389.6	-475.7
Cu63	-1104.1	1631.7	427.0	-30.3	1901.3	3430.4	-1055.1	-1172.1	-1084.2	109.5	-560.9	-677.0
Zn64	1211.7	2553.8	957.9	2965.4	5270.5	4099.8	-865.1	516.4	3876.0	1590.6	203259.3	-275.4
Ag107	167.8	36.9	2104344.3	485.6	553.8	626.3	72.5	1283.2	71.5	113.1	180.4	49.9
Cd114	1.0	-36.3	-24.4	-0.9	12.0	9826.2	-68.1	258.8	-11.1	160139.4	706.1	528.4
Ba138	624.7	25560.5	8738.4	1754.8	11915.2	3911.3	2950.7	191.8	10057.7	2325.2	3879.5	691.5
Pb208	1337.3	6997.7	4382.7	2424.8	14370.3	14225.3	-751.8	-2553.5	563.3	2152.5	-302.6	958.6
I127	-9.0	-1.2	38.8	34768.6	1062.2	-150.0	-121.9	257.5	-317.0	-341.3	200.9	-45.3
Na23	-25803.0	120646.7	248499.8	18450.5	199256.8	125424.4	-32403.5	16273.5	-72581.9	85805.5	-68654.6	55423.2
Mg24	-542.4	62372.5	4998.7	35170.3	60166.3	200248.5	-1046.6	-6227.5	-11491.8	-7462.2	-7318.4	447811.1
Si28	55417.5	174654.6	107860.6	128802.0	417945.8	310193.8	89464.8	100076.1	41564.3	5318.5	29241.8	-13009.8
Sn115	1066.8	2653.6	373.8	485.1	2642.9	9165.0	599.4	468.2	263.0	1471.6	571.9	354.7
Sn117	-76.1	-25.6	197.5	266.9	31.9	119421.8	23.8	64.4	-93.7	402.5	190.8	-84.2
Cd111	-17.6	-31.3	-33.1	-6.1	-25.1	-18.1	-26.9	98.8	6.0	67600.3	281.6	308.8
Zn67	-55.8	217.5	-81.9	517.7	246.3	343.8	-199.4	41.3	-134.3	279.4	18931.1	-147.1
Fe54	28035.1	35995.6	15303.1	6104.8	63023.9	155550.2	-180.4	7106.5	-5988.2	-14789.6	-13519.8	-11424.9
Se74	1.2	2707.2	16.9	16.7	25.3	11.3	-6.3	-12.5	-12.1	1.9	-4.3	-3.8
Cd106	43.4	11.9	6.9	48.5	774.6	-10.6	143.1	10.6	82.2	5945.0	81.0	25.5
Cd116	-204.5	1640.5	513.8	581.4	-70.0	218939.4	64.4	72.5	-338.4	44364.6	556.2	-31.1
Mg25	2060.0	16280.1	1501.4	2169.5	6028.5	11090.3	882.3	-1003.9	-456.1	-582.5	-481.7	57182.9

Table 12: The ratio of element Vs interference

Element/Interference	Ratio	Percentage
Cr53/Ag107	0.000028	0.0028%
64Zn/127I	0.085289	8.5289%
64Zn/28Si	0.012611	1.2611%
57Fe/115Sn	2.410655	241.0655%
58Ni/115Sn	0.295733	29.5733%
59Co/117Sn	0.000729	0.0729%
58Ni/116Cd	0.011612	1.1612%
107Ag/67Zn	0.009530	0.9530%

Table 13: The ICP-MS response/intensity of the six airborne particulate samples

	CA18	CA21	CA22	KS12	KS22	KS26	Average
Al27	388867.2	1033661.9	792813.5	435691.2	767042.5	578072.6	666024.8
Cr52	8025.2	8021.3	9848.0	40824.4	20209.2	24953.2	18646.9
Cr53	699.1	902.0	848.8	1228.5	1197.1	2178.8	1175.7
Mn55	31973.9	64469.5	38450.2	43924.2	48945.3	86520.9	52380.7
Fe57	47694.0	63257.4	53508.0	51985.4	68833.6	88855.2	62355.6
Co59	772.1	1570.2	687.4	2282.4	1945.5	3205.1	1743.8
Ni58	13350.7	17067.4	10502.2	26244.8	22619.0	39548.9	21555.5
Cu63	57862.4	153086.1	56989.6	259917.7	160370.5	119360.5	134597.8
Zn64	11127.8	17045.7	16447.2	38385.8	17682.7	24702.8	20898.7
Ag107	106.8	226.4	248.0	319.3	147.6	402.0	241.7
Cd114	236.9	288.9	508.1	1066.9	847.9	850.0	633.1
Ba138	213504.7	292674.8	237884.3	346428.7	449939.3	506079.8	341085.3
Pb208	76455.7	84977.6	89523.1	168208.5	120579.6	168207.7	117992.1
I127	4403.6	7343.0	8881.6	6025.4	5833.6	8118.8	6767.7
Na23	7123352.9	2451365.3	2077565.1	49916119.5	33244436.7	37794033.3	22101145.5
Mg24	234821.0	281980.8	239789.9	217911.0	320909.8	243132.0	256424.1
Si28	211949.1	479605.6	412207.0	342078.4	330276.0	334231.5	351724.6
Sn115	338.7	269.4	312.1	972.7	333.2	432.6	443.1
Sn117	1315.3	1418.0	2049.8	3912.3	6086.9	4387.4	3195.0
Cd111	26.9	60.7	127.9	295.1	126.2	167.5	134.0
Zn67	1054.4	1777.8	1926.2	3384.3	1793.0	2434.4	2061.7
Fe54	97292.8	172461.7	126698.0	157466.3	205282.6	267274.0	171079.2
Se74	160.3	69.6	126.1	296.3	430.5	327.1	235.0
Cd106	4.8	34.4	158.1	109.2	30.3	128.4	77.5
Cd116	2831.8	2770.8	3443.9	7356.6	11281.6	8500.7	6030.9
Mg25	25202.4	33889.4	26022.7	20822.8	34504.6	29046.0	28248.0

The exact intensities are shown in the **Table 14**.

Table 14: The results of interference in the six samples

	CA18	CA21	CA22	KS12	KS22	KS26	Average
Int. of Cr53	699.1	902.0	848.8	1228.5	1197.1	2178.8	1175.7
Int. of Ag107	106.8	226.4	248.0	319.3	147.6	402.0	241.7
Ratio*Int. of Ag107	0.00298	0.00632	0.00692	0.00891	0.00412	0.01122	0.00675
Exact int. of Cr53	699.1	902.0	848.8	1228.5	1197.1	2178.8	1175.7
Percentage	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%
Int. of Zn64	11127.8	17045.7	16447.2	38385.8	17682.7	24702.8	20898.7
Int. of I127	4403.6	7343.0	8881.6	6025.4	5833.6	8118.8	6767.7
Ratio*Int. of I127	375.6	626.3	757.5	513.9	497.5	692.4	577.2
Exact int. of Zn64	10752.2	16419.5	15689.7	37871.9	17185.2	24010.3	20321.5
Percentage	96.6%	96.3%	95.4%	98.7%	97.2%	97.2%	97.2%
Int. of Zn64	11127.8	17045.7	16447.2	38385.8	17682.7	24702.8	20898.7
Int. of Si28	211949.1	479605.6	412207.0	342078.4	330276.0	334231.5	351724.6
Ratio*Int. of Si28	631.9	3031.3	2854.1	3049.6	1361.3	3751.4	2373.3
Exact int. of Zn64	10495.8	14014.4	13593.1	35336.3	16321.4	20951.4	18525.3
Percentage	94.3%	82.2%	82.6%	92.1%	92.3%	84.8%	88.6%
Int. of Fe57	47694.0	63257.4	53508.0	51985.4	68833.6	88855.2	62355.6
Int. of Sn115	338.7	269.4	312.1	972.7	333.2	432.6	443.1
Ratio*Int. of Sn115	816.6	649.5	752.4	2344.9	803.3	1043.0	1068.3
Exact int. of Fe57	46877.5	62607.9	52755.6	49640.5	68030.3	87812.3	61287.4
Percentage	98.3%	99.0%	98.6%	95.5%	98.8%	98.8%	98.3%
Int. of Ni58	13350.7	17067.4	10502.2	26244.8	22619.0	39548.9	21555.5
Int. of Sn115	338.7	269.4	312.1	972.7	333.2	432.6	443.1
Ratio*Int. of Sn115	100.2	79.7	92.3	287.7	98.5	127.9	131.1
Exact int. of Ni58	13250.5	16987.7	10409.9	25957.1	22520.5	39420.9	21424.4
Percentage	99.2%	99.5%	99.1%	98.9%	99.6%	99.7%	99.4%
Int. of Co59	772.1	1570.2	687.4	2282.4	1945.5	3205.1	1743.8
Int. of Sn117	1315.3	1418.0	2049.8	3912.3	6086.9	4387.4	3195.0
Ratio*Int. of Sn117	1.0	1.0	1.5	2.9	4.4	3.2	2.3
Exact int. of Co59	771.2	1569.2	685.9	2279.6	1941.1	3201.9	1741.5
Percentage	99.9%	99.9%	99.8%	99.9%	99.8%	99.9%	99.9%
Int. of Ni58	13350.7	17067.4	10502.2	26244.8	22619.0	39548.9	21555.5
Int. of Cd116	2831.8	2770.8	3443.9	7356.6	11281.6	8500.7	6030.9
Ratio*Int. of Cd116	32.9	32.2	40.0	85.4	131.0	98.7	70.0
Exact int. of Ni58	13317.8	17035.2	10462.2	26159.4	22488.0	39450.2	21485.5
Percentage	99.8%	99.8%	99.6%	99.7%	99.4%	99.8%	99.7%
Int. of Ag107	106.8	226.4	248.0	319.3	147.6	402.0	241.7
Int. of Zn67	1054.4	1777.8	1926.2	3384.3	1793.0	2434.4	2061.7
Ratio*Int. of Zn67	10.0	16.9	18.4	32.3	17.1	23.2	19.6
Exact int. of Ag107	96.7	209.4	229.6	287.0	130.5	378.8	222.0
Percentage	90.6%	92.5%	92.6%	89.9%	88.4%	94.2%	91.9%

The exact intensity of the analyzed elements which are affected by interference can be calculated by subtract the estimated intensity caused by interference, and the concentration that interfered can subsequently be obtained. In detail, that is to say, the exact intensity of the analyte element equals to the measured intensity value minus the interference value which can be calculated by using the ratio/percentage shown in the **Table 12,** multiplied by the interfering element's intensity measured in the sample. The equations are shown below:

$$I_{exact} = I_{measured} - \text{Ratio} \times I_{interfering} \qquad (iv)$$

How much the results (the concentration in the air) may be interfered mainly depends on two factors: one is the ratio (element/interference), the other is the concentration or intensity of the interfering elements measured in the sample. From the results, Zn64 and Ag107 are interfered a little by their interfering elements. Others show little problem with the interference.

4.3.3 Distribution in filters

To check whether the airborne particles are distributed homogenously, different parts of a sample were analysed. The ICP-MS response (intensity VS time/distance) of the measurement is presented in **Figure 8**. Each peak is represent a section of the sample. The values in between are background signal of ICP-MS that without Laser sampling.
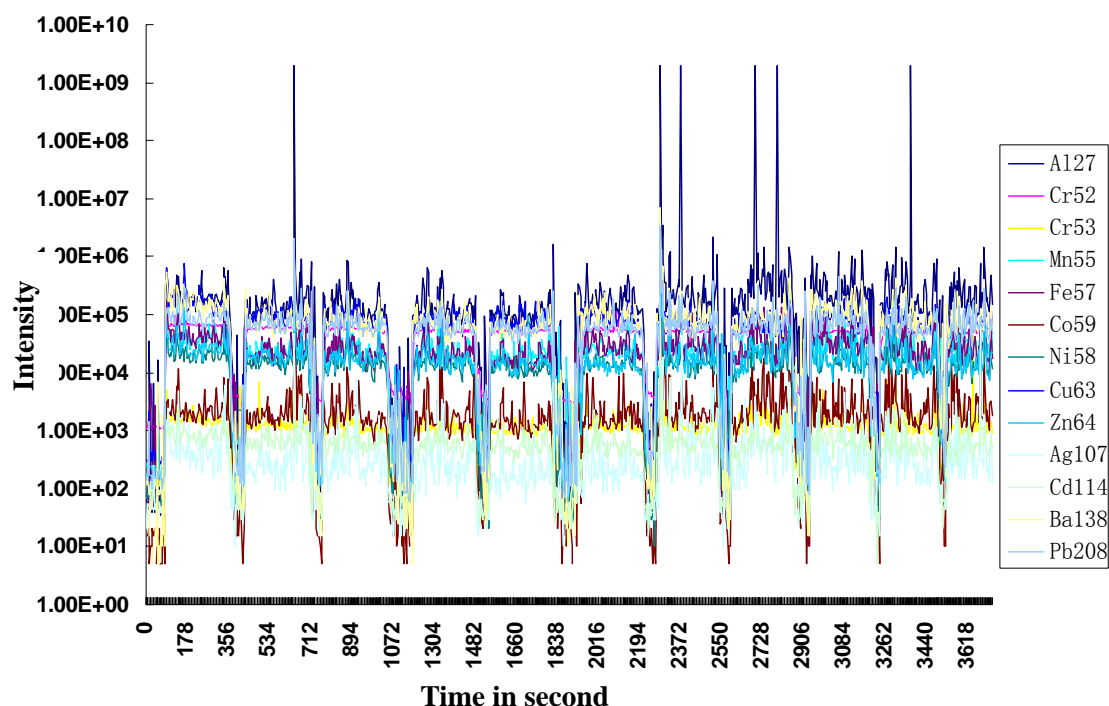

Figure 10: The ICP-MS signals of Al27, Cr52, Cr53, Mn55, Fe57, Co59, Ni58, Cu63, Zn64, Ag107, Cd114, Ba138 and Pb208 by measuring various part of sample Kenmore1.2

The average for each peak, the standard deviation and the relative standard deviation are made as shown in the **Table 15**:

Table 15: The average, Standard deviation and relative standard deviation of the measured sample Kenmmore1.2 for showing the particle sample distribution in filters

	Average	Standard Deviation	Relative Standard Deviation
Al27	233623	75924	32.5%
Cr52	55032	4675	8.5%
Cr53	1505	343	22.8%
Mn55	36595	8633	23.6%
Fe57	37222	9985	26.8%
Co59	2929	772	26.4%
Ni58	16259	2460	15.1%
Cu63	97792	34385	35.2%
Zn64	20536	4596	22.4%
Ag107	798	617	77.2%
Cd114	664	96	14.5%
Ba138	102052	30527	29.9%
Pb208	75834	11225	14.8%

Silver is the least homogenous element in the filter. Other elements have a relative standard deviation between 20% and 30, except for Al and Cu which are less homogenous, and Pb, Cd and Ni (the signal for Cr52 is likely to be essentially the result of ArC interference at mass 52).

4.3.4 Comparison between blank gas and blank filter

Figure 9 provide signal intensities for blank gas and blank filter material. There are significant difference between blank gas and blank filter. That is to say, the filter contains a certain amount of metals which may affect the results of the sample, which proves that during the calculation, the value of the sample must be subtracted by the blank filter value. Otherwise the results would be inaccurate.
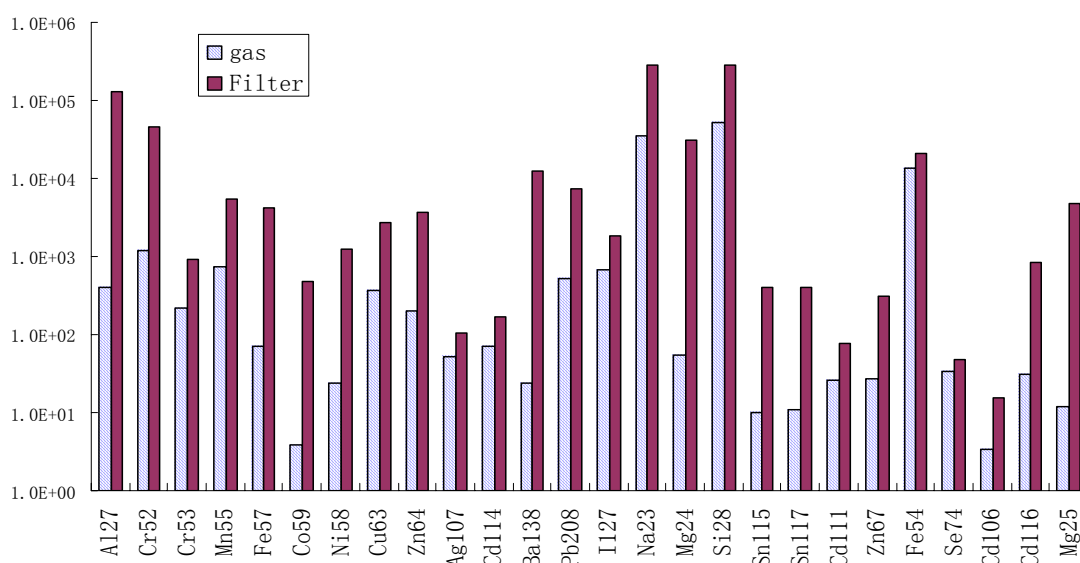

Figure 11: the comparison between blank gas and blank filter

5. Conclusion

Laser ablation inductively couple plasma mass spectrometry (LA-ICP-MS) is a convenient and sensitive technique for direct solid analysis. A method based on LA-ICP-MS has been developed for the analysis of airborne particulate matter samples collected on cellulose filters. The standard can be prepared by dropping the coloured standard solution on the blank filter. Rhodamine B is one of the suitable colorants for dye. The satisfying results of the calibration show a good future of this dried-droplet standard preparation method for the analysis of airborne particles and other particles on filters. The method was applied to the analysis of airborne particles collected in Boston. Detection limits were found to be suitable for the analysis of Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Ba and Pb in Boston air and interference were found to be limited. The method reduces the analysis time and minimises the sample preparation and is therefore suitable for the screening of element concentrations in urban air.

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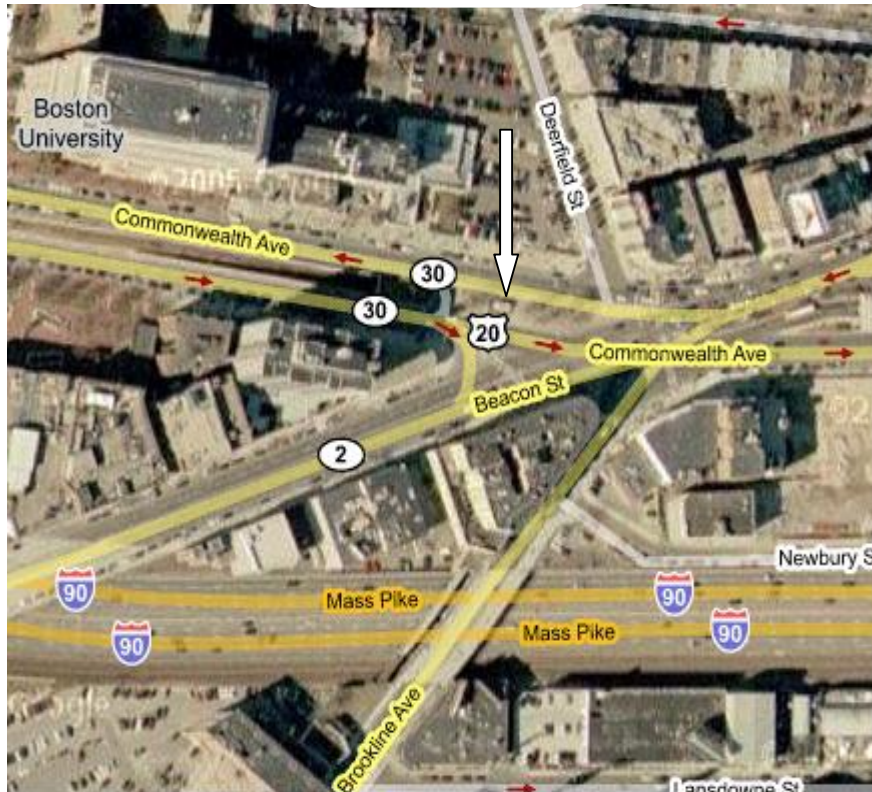
Air sampling Locations – Boston (a)

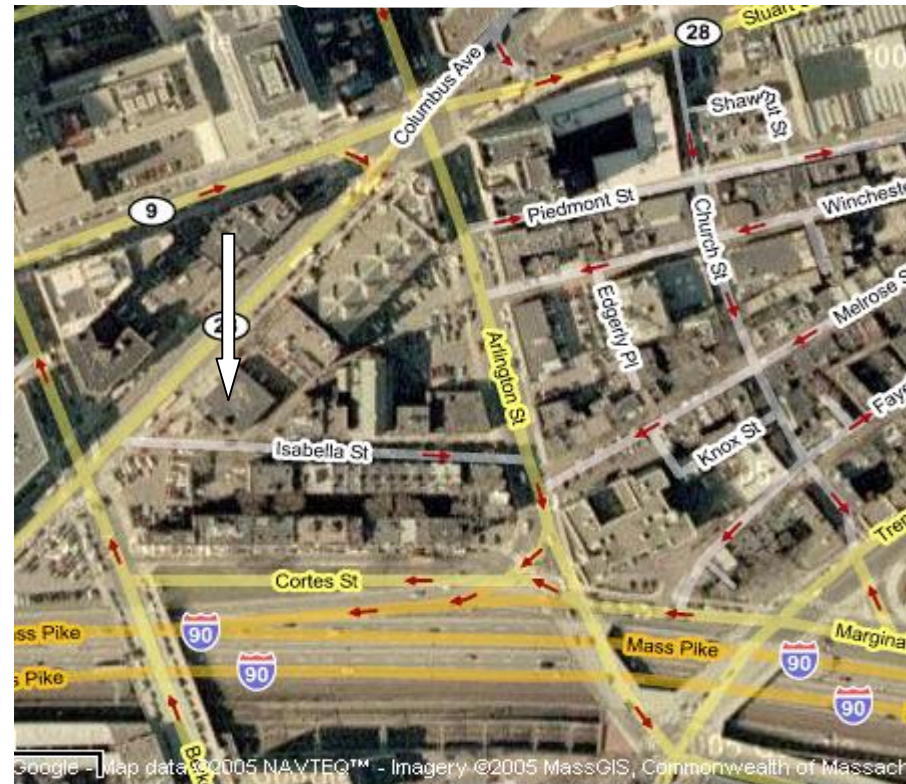# Air sampling Locations – Boston (b)

Kenmore Sq.   **Columbus Ave.**

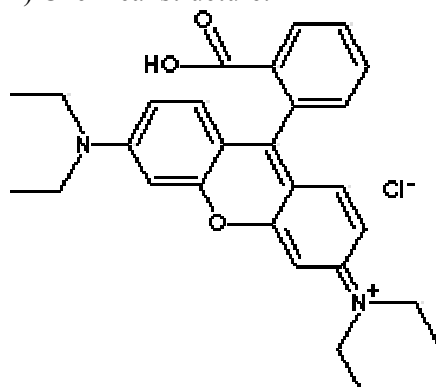**Appendix 2: Rhodamine B**

Description

1) Molecular Formula: C28H31O3N2Cl

2) Chemical structure:

3) Molecular Weight: 478.5

4) Physical and chemical properties:
Appearance is glisten bright green or violet flaky crystal. Soluble in water and the solution shows pink. It is leuco precipitate when dissolved in sodium hydroxide solution.

5) Application:
For dyeing of paper, acrylic fibers, silk, leather and feather; Also can be used in food and analytical reagent of some metals.

Appendix 3: The Basic interferences of the analyte metals

	Basic interference
Al27	53Cr++, 54Cr++, 54Fe++, 11B16O, 9Be18O, 55Mn++
Cr52	103Rh++, 104Pd++, 104Ru++, 36S16O, 12C40Ar, 36Ar16O, 35Cl17O, 105Pd++
Cr53	105Pd++, 106Pd++, 106Cd++, 37Cl16O, 13C40Ar, 35Cl18O, 36Ar16O1H, 107Ag++
Mn55	109Ag++, 110Cd++, 110Pd++, 39K16O, 15N40Ar, 37Cl18O, 38Ar16O1H, 19F36Ar, 111Cd++
Fe57	113In++, 113Cd++, 114Sn++, 114Cd++, 41K16O, 19F38Ar, 40Ar17O, 40Ca17O, 39K18O, 40Ar16O1H, 115Sn++, 115In++
Co59	117Sn++, 118Sn++, 43Ca16O, 23Na36Ar, 19F40Ar, 41K18O, 40Ar18O1H, 119Sn++
Ni58	115Sn++, 115In++, <u>Fe</u>, 116Sn++, 116Cd++, 42Ca16O, 20Ne38Ar, 22Ne36Ar, 40Ar18O, 40Ca18O, 40Ar17O1H, 40Ar16O2H, 117Sn++
Cu63	125Te++, 47Ti16O, 25Mg38Ar, 27Al36Ar, 126Te++, 126Xe++, 23Na40Ar, 45Sc18O, 40Ar17O1H, 40Ar16O1H, 117Sn++
Zn64	127I++, <u>Ni</u>, 48Ti16O, 28Si36Ar, 26Mg38Ar, 24Mg40Ar, 48Ca16O, 128Xe++, 46Ti18O, 128Te++, 23Na23Na17O1H, 23Na23Na16O2H, 14N18O16O16O, 129Xe++
Ag107	69Ga38Ar, 67Zn40Ar, 71Ga36Ar, 91Zr17O, 90Zr17O, 89Y18O
Cd114	76Se38Ar, 74Ge40Ar, 76Ge38Ar, 78Se36Ar, 74Se40Ar, 78Kr36Ar,98Ru16O, 98Mo16O, <u>Sn</u>, 96Mo18O, 96Ru18O
Ba138	100Ru38Ar, 98Ru40Ar, 98Mo40Ar, 100Mo38Ar, 102Ru36Ar, 102Pb36Ar, 122Te16O, 122Sn16O, 120Sn18O, 121Sb17O, <u>Ge</u>, <u>La</u>
Pb208	168Er40Ar, 168Yb40Ar, 170Yb38Ar, 170Er38Ar, 172Yb36Ar, 192Pt16O, 192Os16O, 190Os18O, 191Ir17O

* The elements with double underline are the ones automatically calculated in the ICP-MS.