The determination of Arsenic in soil by ICP-OES

by

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SYNOPSIS

Arsenic has always played a major role in the environment and human life in general. From its earliest uses, in ancient times, as a poison to its most recent use, in medicine, as an anti-leukemia agent, this metal has fascinated mankind. This fascination has already yielded several surveys on its toxicity, concentration, source and specie. However, some approaches have not been fully explored. One of these is its occurrence in Phosphate bearing rocks and subsequent possible contamination of fertilizers derived from these rocks. To this end, a new variation of a speciation mechanism used, solvent extraction followed by ion-exchange, has been developed. Although this method has mainly been used in connection with marine samples, in this dissertation, it has been applied to solid samples. The levels of arsenic were then determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). Phosphate bearing rocks, commercial fertilizers and soils were digested in HCl and speciated out as As(III), As(V), Mono-Methyl Arsenic acid (MMAA) and Dimethyl Arsenic acid (DMAA). The effect of different organic phases were examined as well as two ion-exchange resins. Phosphoric acid, being an intermediate stage in the manufacture of diverse fertilizers, was also investigated. Due to the close relationship between arsenic and phosphorus, some steps in the method had to be reversed in order to yield better results. The resulting samples were analysed at two wavelengths, ie 188.979nm en 193.696nm. Although the values obtained at the two wavelengths differ by between 0.5mg/kg and 1.5mg/kg, a simple t-test proves that the values are reconcilable. A micro-concentric nebuliser was studied regarding its aerosol particle size, with a μ-LASER-particle-analyser, and the detection limit of arsenic. The second part of this study could not be completed due to the loss of the ICP. The following four nebulisers were compared: Micro-Concentric Nebuliser (MCN), Meinhard Nebuliser, V-groove Nebuliser and a Cross-flow Nebuliser. Due to their similar design, the MCN and Meinhard nebulisers have similar characteristic, the main differences being in their operating characteristics, ie regarding particle size and background intensity. As the inside diameter of the MCN is only 0.2μm special glassware had to be developed to insure that the MCN does not become blocked.

SAMEVATTING

Arseen het nog altyd 'n belangrike rol in die natuur en menslike lewe oor die algemeen gespeel. Hierdie metaal het die mens van die begin af betower, van die vroegste gebruik, in die verre verlede, as gifstof tot die hedendaagse gebruik in die mediese wêreld as anti-leukemie middel. Hierdie betowering het reeds gelei tot vele studies na die giftigheid, konsentrasie, bronne en chemiese vorme van arseen. Sekere benaderings is egter nie ten volle bestudeer nie. Een van dié, is die voorkoms van arseen in fosfaatbevattende rots en die gevolglike moontlike besoedeling van kunsmis wat vanuit die rotse vervaardig word. Vir hierdie doel is 'n nuwe variasie van 'n bestaande metode om arseen in sy verskillende chemiese vorme te verkry, gebruik; naamlik oplosmiddel-ekstraksie gevolg deur ioon-uitruiling in 'n gepaste kolom. Alhoewel die metode meestal in die ontleding van seemonsters gebruik word, word die metode tydens hierdie verhandeling op vastetoestand-monsters toegepas. Die arseenvlakke is met behulp van Induktief Gekoppelde Plasma Optiese Emissie Spektroskopie (IGP-OES) bepaal. Fosfaat-bevattende rots, bedryfskunsmis en grondmonsters is in HCl opgelos en geskei in die volgende chemiese vorme: As(III), As(IV), monometielarseensuur (MMAS) en dimetielarseensuur (DMAS). Die effek van verskillende organiese fases, sowel as twee ioon-uitruilingsharse is ondersoek. Fosforsuur, as tussenproduk in die vervaardiging van verskeie kunsmisstowwe, is ook ondersoek. Weens die nabye verwantskap tussen arseen en fosfor moes verskeie stappe in die gebruikte metode omgeruil word, om beter resultate te lewer. Die verkrygde monsters is by twee golflengtes, 188.979nm en 193.696nm, ontleed. Alhoewel daar 'n verskil van 0.5 – 1.5mg/kg in die waardes is wat by die

verskillende golflengtes verkry word, toon 'n eenvoudige t-toets aan dat die waardes versoenbaar is. 'n Mikro-konsentriese newelaar is ondersoek ten opsigte van die sproei-deeltjiegrootte, met behulp van 'n μ–LASER-deeltjiegrootte-ontleder en ook ten opsigte van die bepaalbaarheid van arseen. Die deel is egter nie voltooi nie, weens verlies aan die IGP. Tydens die deel van die studie is vier newelaars, die Mikro-Konsentriese Newelaar (MKN), Meinhard Newelaar, V-Groef Newelaar en 'n Kruis-Vloei Newelaar vergelyk. Weens hulle soortgelyke ontwerp is die eienskappe van die MKN en Meinhard newelaars ook soortgelyk, met die grootste verskille in hul bedryfseienskappe, naamlik ten opsigte van deeltjiegrootte en agtergrondsterkte. Spesiale glasware moes ontwikkel word, om te voorkom dat die MKN verstop word, aangesien die binne deursnee van die MKN slegs 0.2μm is.

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CHAPTER 1

INTRODUCTION

1.1 ICP as an analytical method

Inductively Coupled Plasma Atomic Emission spectrometry (ICP-AES) is a technique used predominantly for the quantitative multi-element analysis of most types of samples, eg. biological and geological materials. It is an ideal technique due to its high dynamic range which allows for the analysis of both major and trace elements from a single sample (i.e. from g/l to µg/l range). Major elements can easily be analysed with high accuracy and precision through internal standardisation and proper calibration procedures. As with many other analytical techniques, trace elements, however, can be more problematic. These problems can be related to the background enhancement and spectral line overlap from concomitant elements. Physical interference can occur during the nebulization process that will affect accuracy and precision. Here again, internal standardisation can be used to rectify the sample transport variation. Sensitive measurements of refractory elements such as B and P are also catered for by this technique through the high temperature of the ICP.

There are two systems available for ICP-AES, simultaneous and sequential. Simultaneous systems have a higher sample throughput as more elements can be analysed for a time period. This is because the wavelengths at which the elements are analysed are preselected in the manufacturing process. A direct result of this however is the lack of control over the analysis. Sequential systems have the advantage of flexibility of wavelength selection. This in effect, allows for variations in analyte

concentrations and matrix types and the removal of interfering peaks by the selection of a different wavelength, with the major drawback of much longer analysis time. As geological materials are generally very complex in composition, several sources of interference can generally be expected in ICP-AES. These can be eliminated by using a high resolution spectrometer, on-line background compensation, predetermined interference coefficients or matrix matched standards. Several methods for background compensation exist, many mathematical, which usually involve scanning a spectral segment on either or both sides of peak positions. Then, the spectrum for each interferent is measured and removed mathematically from the analyte signal.

Any productive spectrometer should, in theory, fulfil these capabilities:

- a high degree of resolution to achieve good separation from nearby spectral lines, thereby reducing inter-element interference
- exhibit high sensitivity through excellent light-gathering and least stray light
- be stable, both mechanically and thermally, ensuring both the precision and repeatability of the analysis and ensuring that the correct wavelength has been selected.
- low detection limits to measure trace elements plus major elements.

As ICP-AES is a very similar spectroscopic tool to flame and graphite furnace atomic emission spectroscopy, the advantages and disadvantages of this technique can best be described though a brief comparison of the three. Although atomic absorption is a stronger phenomenon than atomic emission, where typically only $1*10^{-6}$ photons emitted by atoms reaches the detector, ICP-AES offers a tremendous narrowing of the detection

limits gap. Species are highly excited due to the high temperatures of the plasma. This translates into extensively populated excited states yielding a simultaneous, intense emission from many lines. Flame and graphite furnaces' emissions are much less intense as the normal operating temperatures of these techniques are characteristically between 2,000 and 3,500 K. More popularly, flame and graphite furnaces operate as absorption spectrometers, as absorption is a stronger phenomenon than emission, through the absorption of light by excited states with low energies less than 3 eV.

The low detection limits achieved by ICP-AES are predominantly due to the large emission signals with respect to the noise of the background of some elements (µg/l sometimes). These detection limits are obviously sample dependant. Therefore, they are easily degraded by difficult matrices, increased background, and by spectral overlaps.

1.2 ARSENIC IN THE ENVIRONMENT

1.2.1 Types of arsenic found in soils and relative toxicity:

Although several forms of arsenic can be found in soils, there are four major groups that are important. These different forms of arsenic can be separated into two major groups, inorganic arsenic in the oxidation states As(III) and As(V) and organo-arsenicals, mono-methyl (MMA)- and dimethyl-arsenic (DMA) acids. These last two arsenic forms are mainly found in an aquatic environment and are thought to be 100 times less toxic than the inorganic forms. These methylated forms are the result of biological transformation of the inorganic species [1,2].

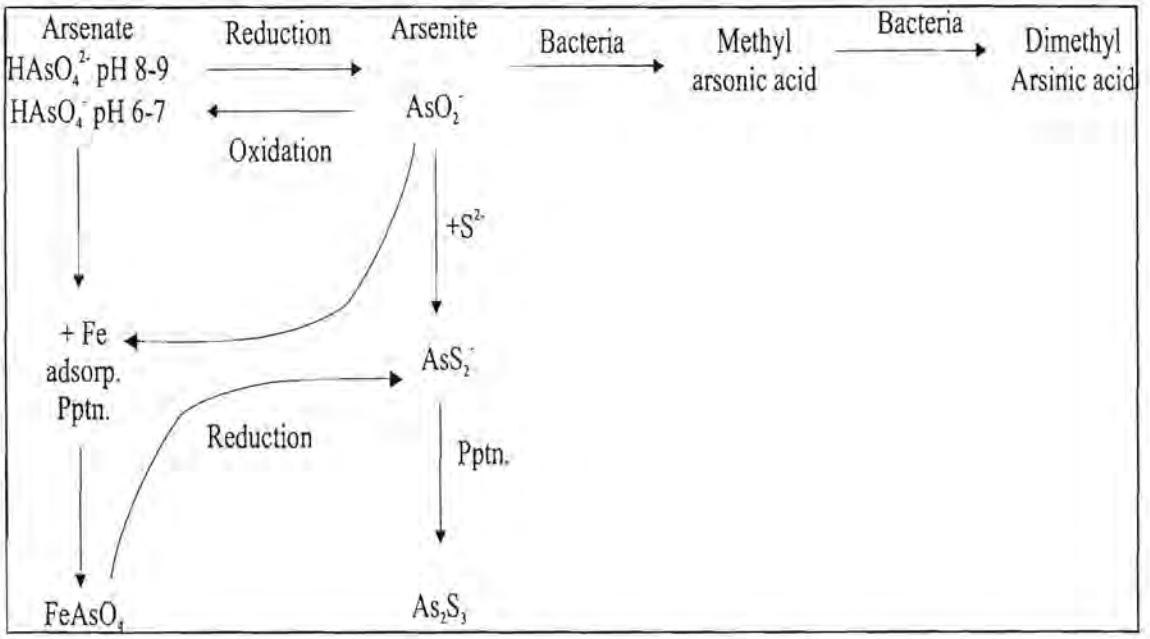

Figure 1: Chemical forms of arsenic and their transformations in soils [1].

The first or most ancient source of arsenic in the environment would be weathering of the parent rock. Indeed, extensive surveys of the levels of arsenic have found that different parent rocks led to varying levels of arsenic in soils. For example, arsenic in soils derived from granite is lower than in those derived from basalt while the level in soil derived from sedimentary rocks may attain a value of 20 to 30 mg/Kg. Furthermore, the amounts found in the earth's crust and shales are 1.8 and 13 mg/Kg respectively which is mainly a result of its accumulation during weathering and translocation in colloid fractions. The average concentration around the world of As is 6 mg/Kg, ranging from 1 to 50 mg/Kg. Arsenic is concentrated in magmatic sulfides and iron ores. The most important ores of arsenic are arsenic pyrites or mispickel, realgar, and orpiment. The arsenic levels in soil enriched in these ores are often higher than in normal soil. The arsenic content of soil may be closely related to the underlying bedrock if the parent materials have not been mixed or redistributed by pedogenetic processes, wind, or glaciation [1].

The second source (and least important) is from geological upheavals such as volcanoes where the average arsenic soil content is about 20 mg/Kg while outside these localities the soil content is closer to 2 mg/Kg [1].

Table 1: Movement of Arsenic in the environment [1].

From:	To:	Approx. Amount ($*10^8$ g/year)
Land	Oceans	3,000
	Atmosphere	1,000
	Biota	300
Atmosphere	Oceans	2,000
	Land	1,000
Oceans	Sediments	2,500
	Biota	1,300
	Dissolved	1,000
Sediments	Land	2,400
Mining, smelting		500
Terrestial biota	Land	300
Volcanoes	Land	54
	Sediments	40
	Atmosphere	3

The third and obviously most recent source of arsenic is anthropogenic. This category can be further broken down into two. These being, direct contamination or rather purpose driven and indirect contamination or incidental [1]. From table 1 it is possible to see that although arsenic has been used by humans, such use is not the predominant cause of movement of arsenic in the environment. Indeed, anthropogenic arsenic pollution tends to occur in localised areas though in some places such as Bangladesh, the ground water can become polluted due to such activities. Table 2 highlights the major

uses of arsenic by humans, which can be seen to encompass most aspects of modern industrial production.

- In the fifties and sixties, arsenic compounds were used as fungicides, pesticides and insecticides (some of which are still in use today). This use is still reflected in the levels of arsenic found in some areas today that can be greater than 100 mg/Kg, especially in orchards.
- The other source, incidental contamination comes from mines, industry and uses of arsenic containing compounds (fertilizers for example) which have not been properly examined. In Japan, the arsenic content of soils was 1475 mg/Kg at 300 yards and 11.15 mg/Kg at nine miles from the chimney of the Obuasi goldmine.

Since the 1920's the recorded world production of Arsenic Trioxide (White Arsenic) has been between 30,000 and 65,000 metric tons with a maximum output of 63,939 in 1970. As recently as 1990, 47,632 metric tons were still being produced despite the well-recorded dangers to human health and the environment [1].

Table 2: Uses of Arsenic in the economy [1].

Sector	Uses
Agriculture	Pesticides, insecticides, defoliants, wood preservatives, debarking trees, soil sterilant
Livestock	Feed additives, disease prevention (swine dysentery, heartworn infection), cattle and sheep dips, algaecides
Medicine*	Antisyphilic drugs, treatment of trypanosomiasis, amebiasis, sleeping sickness
Electronics	Solar cells, optoelectronic devices, semiconductor applications, light-emitting diodes (digital watches)
Industry	Glassware, electrophotography, catalysts, pyrotechnics, antifouling paints, dyes and soaps, ceramics pharmaceutical substances
Metallurgy	Alloys (automotive body solder and radiators), battery plates (hardening agents)

* Arsenic still used for medicinal purposes in some developing countries

1.2.2 Properties of arsenic useful in analysis

Although arsenic has several properties that are useful in specific analytical techniques, some properties (e.g. thermodynamic, ease of redox) are useful in all. Foremost among these are the differing chemical properties of the various oxidation states. For example, arsenite, As(III) can be easily reduced to arsine, which has a low boiling point (-55°C) and therefore can easily be distilled from complex sample matrices. This, coupled with the fact that arsenate, As (V), needs to be reduced prior to hydride generation gives us a powerful tool for speciation. The methylated forms of arsenic can also directly produce arsines (under reducing conditions) which have widely separated boiling points, thus allowing for further speciation through distillation.

Thermodynamic considerations also play a major role in analysis. By addition of simple oxidizing or reducing agents such as KI or KIO_3, arsenite and arsenate can easily be interconverted although arsenate is the more thermodynamically stable form. This means that Arsenite can be converted to arsine along with the methylated arsenic, leaving arsenate behind.

Other properties that play a major role in the speciation of arsenic are the easy conversion of arsenite into arsenic trichloride by treatment with strong hydrochloric acid. This arsenic trichloride, being covalent in nature is soluble in organic solvents while arsenate, which doesn't react with HCl, is not extracted by an organic solvent. Furthermore, arsenite can form complexes with sulfur compounds which gives another route for

speciation. Arsenate on the other hand can be studied with colorimetry by complexing with molybdic acid and reduced to give a characteristic blue colour [1].

1.2.3 Soil conditions:

1.2.3.1 Type of soil and parent rock type

As mentioned earlier, the principal factors influencing the concentration of elements in soils are the parent rock and human activities. Studies have shown that arsenic contents are positively correlated to the level of clay and negatively correlated to the level of sand in the soil. Therefore, two main comparison points must be taken into account: the parent rock and soil texture, especially as typically, the arsenic content is related to the concentration of organic material [1].

1.2.2.2 pH and Eh of soil

Although these values do not affect the concentration of arsenic found in soils as such, they do influence the relative abundance of the various species of As. As(III) is much more toxic and soluble than As(V) and more mobile. Studies of the relationship between solubility and Eh and pH have shown that soluble arsenic increased significantly with diminishing Eh and increasing pH. Furthermore, arsenic adsorption is related to the pH level, with a decrease in sorption of 46.5 µg As/g soil with a pH change from 5.2 to 9.4. The quantity of adsorbed arsenic by soil was maximum at pH 6 to 8 for arsenite and at pH 4 for arsenic acid [1].

1.2.3.3 Presence of other metals

In a mineral rich region, the levels of arsenic may be much higher as As is associated with several minerals. Of particular interest are iron mines as arsenic is often found as arsenopyrite and in copper containing compounds. During the formation of sedimentary rocks, arsenic is carried down by precipitation of iron hydroxides and sulfides. Therefore, iron deposits and sedimentary iron ores are rich in arsenic. Because arsenic is very similar in chemistry to P but also can have more oxidation states, it can insert itself into many different lattices, such as S compounds. Hydrous oxides of Al, Fe, and Mn affect arsenic surface reactions [1]:

(M=metal)

$$M\text{-}OH + H_20 \rightleftarrows M\text{-}OH_2^+ + OH^-$$

$$M\text{-}OH_2^+ + H_2AsO_4^- \rightleftarrows M\text{-}OH_2^+\cdots H_2AsO_4^-$$

or

$$M\text{-}OH_2^+ + H_2AsO_4^- \rightleftarrows MHAsO_4 + H_2O$$

Addition of As(III) as $HAsO_2$ to untreated or MnO_2-coated sediments result in oxidation to As(V) or adsorption onto the surfaces of the oxides. The oxidation of As(III) by MnO_2 proceeds as:

$$HAsO_2 + MnO_2 \rightarrow (MnO_2)\cdot HAsO_2$$

$$(MnO_2)\cdot HAsO_2 + H_20 \rightarrow H_3AsO_4 + MnO$$

$$H_3AsO_4 \rightarrow H_2AsO_4^- + H^+$$

$$H_2AsO_4^- \rightarrow HAsO_4^{2-} + H^+$$

$$(MnO_2)\cdot HAsO_2 + 2\ H^+ \rightarrow H_3AsO_4 + Mn^{2+}$$

If the MnO_2 has much iron oxide coating, large amounts of arsenic are adsorbed; pure iron oxide is an even more effective adsorbent. Furthermore, iron oxides adsorb arsenic even more strongly than do manganese oxides. The ability of amorphous iron oxides to adsorb arsenic strongly is related to their loose and highly hydrated form, allowing other hydrated ions to diffuse freely throughout the structure without being restricted to external surface sites, as in more crystalline solids. As(V) is less strongly adsorbed than As(III).

Anions when present, especially phosphate ($H_2PO_4^-$) can effectively compete with arsenic for adsorption sites, particularly aluminum and iron oxide surfaces. About 60% of the adsorbed As(V) and 70% of the adsorbed As(III) were displaced by $H_2PO_4^-$ in a solution of 10^{-6} M phosphate. Other anions were less effective in displacing arsenic, with the order of effectiveness decreasing for As(V) of $H_2PO_4^- > H_2AsO_4^- > SO_4^{2-} > CO_3^{2-}$ and for As(III) of $H_2PO_4^- > H_3AsO_3 > F^- > SO_4^{2-} > CO_3^{2-}$. Phosphate substantially suppressed arsenic adsorption, but this varied from soil to soil [1,2,4].

The role of calcium in arsenic fixation is less pronounced than the role of aluminium or iron as calcium arsenate is more soluble than aluminium or iron arsenate. However, plant growth on soils containing toxic levels of arsenic does not improve with liming, since lime does not reduce the availability of arsenic by formation of calcium arsenate. Arsenic forms sparingly soluble compounds with Ca^{2+} with a log K value of -18.17.

1.2.3.4 Depth factors

The quantity of arsenic which is found in soils depends on many factors. For example, arsenic is not very mobile. It tends to remain in one place unless displaced by other chemicals such as phosphates. However, when considering fields that are or have been in use several factors must be considered. The first one being fertilization, as many chemical fertilisers are phosphate rich. Also, if the field is ploughed then the depth to which it is ploughed is important as ploughing causes the soil to be mixed. Therefore the results over this depth should be similar and may not be true values when compared with unused soil.

Another reason that the depth of sampling is important is that recent laboratory studies have shown that arsenic deriving from Lead Arsenate can be displaced by phosphate introduced by using fertiliser. This would then mean that the level of As in the top soil would be less than the expected value and that the level in the subsoil would be greater than the expected value. While this means that the phytotoxicity and human health hazards associated with exposure to high As concentrations in topsoil are generally reduced, this can lead to a contamination of shallow water tables which obviously caries its own risks [1,5].

1.2.3.5 Other considerations

When studying the water soluble part of As, the values may be lower during the rains. This value could be higher in the summer for the first 5 cm due to atmospheric deposition. Also the frequency of fertilising should be considered and the time elapsed since the last fertilising. The more fertilised the field, the higher the value may be (if the fertiliser is the source of Arsenic). Other factors are obviously the use of pesticides,

herbicides or fungicides and previous use of the soil. Fields which were orchards in the 50's and 60's might have much higher levels of As [4].

Plant availability: Not all As in the soil is available to plants. This is an important factor as As has similar characteristics to P and therefore can be easily taken up by plants. However, most plants cannot tolerate a high level of As and die, should their intake be too great. However, while feeding some animals may take in As directly from the soil. The age and health of the plant are important (ie, must not compare apple trees and wheat) [1].

1.2.4 Extraction methods:

There are several methods of extraction possible. The particular one used depends on what information is required. The two main methods used can be classified as follows: sequential leaching or total content. The sequential leaching procedure, highlighted in table 3, is based on speciating the As into its various natural phases, these being: water soluble, exchangeable, carbonate, easily reducible, moderately reducible, organic matter and sulphide and the residual mineral. Further subdividing these fractions into the different species of Arsenic (III, V, MMA, DMA) may prove to yield too small quantities of As to measure without concentration. The total content procedure, which is the favourite among the articles, involves "digesting" the soil in HNO_3 or HCl.

Table 3: Fractional extraction of Arsenic from soils [1].

Arsenic fraction	Extraction Solution
Water soluble	H_2O (distilled)
Exchangeable	1 mol/l NH_4 acetate, pH 7, 1:20 (sample: solution), 20°C.
Carbonate	1 mol/l Na acetate, pH 5, 1:20, 20°C
Easily reducible	0.1 mol/l hydroxylamine hydrochloride, 0.1 mol/l HNO_3, pH 2, 1:100
Moderately reducible	0.2 mol/l NH_4 oxalate, 0.2 mol/l oxalic acid, pH 3, 1:100
Organic matter and sulfide	H_2O_2 (0.30 g/g), HNO3, pH 2, 85°C, NH_4 acetate (1 mol/l)
Residual mineral	$HF/HClO_4$

1.2.5 Speciation methods:

As mentioned earlier, arsenic has several useful properties which can be of great assistance during speciation. The easiest method (used mainly when the two inorganic forms of As (III, V) need to be speciated), is a simple conversion of As (III) into $AsCl_3$ by simple addition of strong HCl (5 - 9 M). This covalent compound can then be extracted into an organic phase such as benzene [1]. In environmental samples, however, the most used method may be hydride generation. Although only arsenite is reduced to arsine by sodium borohydride at pH 4 to 9, all four forms of arsenic can be reduced at a lower pH. The arsines produced can be collected by a cold trap and speciated by distillation. A more efficient way to achieve separation would be to use gas chromatography at this stage with a careful control of the experimental conditions to avoid a rearrangement of the arsines.

The importance of ion exchange in the study of environmental samples cannot be stressed enough. Used properly, this technique can serve as an online pre-concentration

system of ultra trace elements and also a reproducible speciation technique, which is not always the case with Hydride Generation. Ion exchange methods can provide high enrichment factors, lower detection limits by separating the metals of interest from the matrix and less interferences from other metals or oxidation states by speciating the various metals and oxidation states. The on-line ion exchange techniques can also offer, in contrast with manual pre-concentration techniques, the advantages in the reduction of both analysis time and required sample volumes, not to mention a high sample throughput. In addition, by working with a closed system, the risk of contamination from open laboratory environment is reduced [3].

Due to the several advantages of ion exchange, several variations of the technique have been developed. For example, the simplest method is to have an anion exchanger and a cation exchanger in separate tubes and to run the arsenic containing solution through both tubes. The various forms of As would be retained by the tubes and can be released with acid or base at specific molarity. This method has one major flaw in that DMAA is defined as the portion of As being eluted from the cation exchanger with a base. This is nonspecific and could cause confusion when dealing with As samples coming from marine animals that appear to contain large amounts of basic As. These compounds may exhibit very similar behaviour to that of DMAA under these conditions [5].

Another method of ion exchange is to pack the column with successive layers of anion and cation exchangers. The solution can then be run through the column and the various forms of As should be separated through their different retention times. The usual order of elution is: As(III), MMA, As(V), DMAA. The main problem with this method is that

the columns will contain much packing and therefore would be subject to a large amount of back-pressure. This can be overcome by using HPLC-type pumps and tube designed to withstand these conditions.

1.2.6 Hydride Generation

Hydride generation has been extensively researched in conjunction with arsenic studies. The main problems associated with arsenic studies have often been the speciation of the various oxidation states of arsenic plus the removal of interferences due to other metals. Indeed, the different toxicity of the inorganic forms alone has been a cause for concern and therefore the need to determine the exact composition of the arsenic in the environment has arisen. For example, As (III) is considered the most toxic form of arsenic while arsenobetaine and arsenocholine are tolerated by living organisms and are commonly found in crustaceans and mollusks such as lobster and shrimp. Although several techniques have been developed over the years to speciate As (III) and As (V) such as solvent extraction, these do not necessarily remove all the interferences from other metals. Occasionally, the use of the wrong solvent and/or pH can even lead to the co-precipitation of the arsenic and the interferent. Other problems are the high risk of sample contamination arising from these techniques that are very labour intensive and a low replication value (high chance of human errors and/or loss of sample due to transferring the sample from one container to another several times). Another problem is the very low concentration levels of the As species in the environment that therefore require the use of highly sensitive techniques.

Many hydride generators can be directly coupled to an ICP-AES system. This step alone reduces the risk of sample loss and contamination. Furthermore, the conditions under which the hydride generation occurs (temperature, pH, ...) can be carefully selected and controlled thus effecting a good speciation of the arsenic compounds and also isolation of the arsenic from the matrices. This method also can be partially automated thus allowing for a higher sample throughput [1,3].

1.3 References

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CHAPTER 2

INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROSCOPY (ICP-AES)

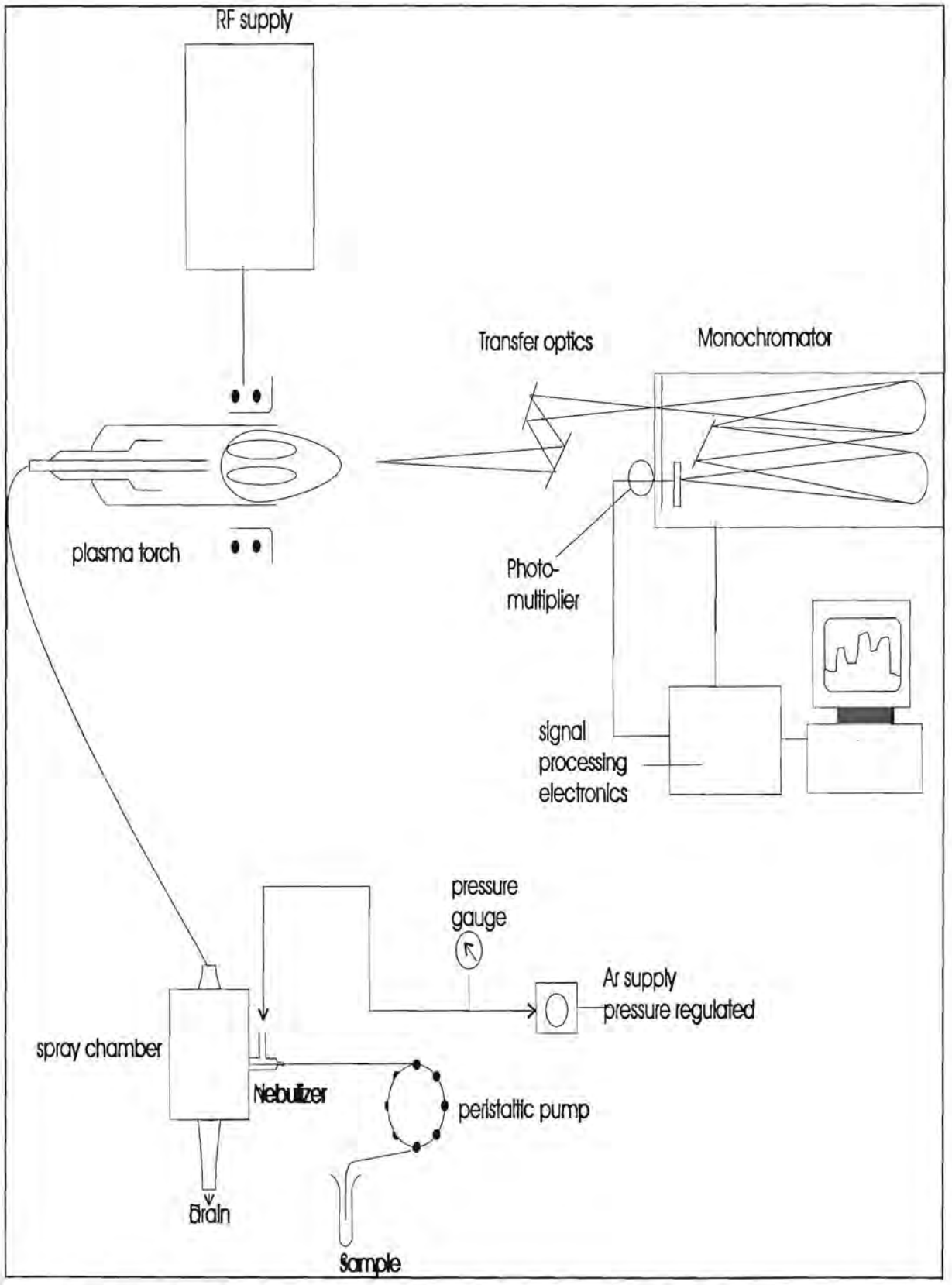
2.1 The theory of ICP-AES

ICP-AES is based, as its name indicates, on the principle of emission. Simply put, excited atoms and ions emit radiation of characteristic wavelength when they return to a ground state. Therefore, by analysing the intensity of the wavelengths present in a spectrum, it is possible to obtain a quantitative analysis of a sample while identifying these wavelengths yields a qualitative analysis.

To this end, an ICP-AES system must comprise of at least a source of excitation and a detector. Figure 1 shows a typical arrangement for an ICP-AES which typically consists of:

- A sample introduction system
- The ICP torch and gas supplies
- A radio-frequency generator
- An optical spectrometer
- Detectors and other electronics
- Computerised instrument control, data collection and analysis

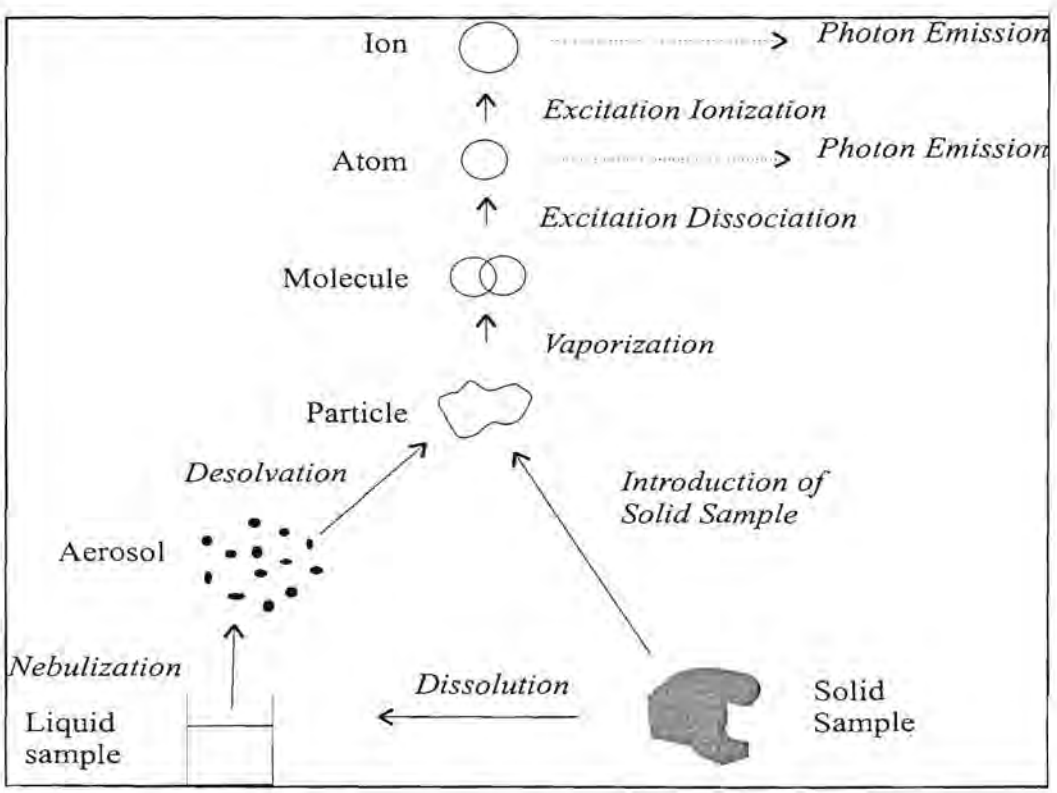
Figure 1: schematic representation of an ICP-AES [1].



2.1.1 Sample introduction

Although most samples used in ICP-AES are in solution form, there are possibilities for the introduction of gas, slurry or solid samples. Samples are most commonly acid digested which minimises and in some cases eliminates interferences due to the sample matrix. In the case of an organic matrix, this procedure has the advantage of improving the detectability of the analyte elements as the energy that would normally be used to destroy the matrix can then be used to excite the analyte. In the case of slurries or solutions, nebulizers are the most common means of sample introduction. The samples is brought to the tip of the nebulizer through the aid of a peristaltic pump where it is converted to an aerosol by Ar gas. The lighter part of the aerosol is then transported to the ICP with the larger droplets removed in the spray chamber to afford an almost homogeneous distribution of analyte elements.

Figure 2: Process of sample introduction and analyte emission [1].



These nebulizers can be subdivided into two classes: pneumatic and non-pneumatic. A pneumatic nebulizer relies on compressed gas to generate the aerosol. These nebulizers are most commonly concentric, cross-flow and V-groove. These are further described in chapter 4. Pneumatic nebulizers have a tend to generate a finer aerosol, i.e. on average smaller droplets, with an increase of the nebulizing gas flow rate [2]. However, they do have a major drawback. Their sample solution capillaries tend to be very narrow, in some cases under 0.5 microns, which tend to be clogged by solutions with high salt contents or high percentages of suspended particulate.

The other category of nebulizers, non-pneumatic nebulizers such as ultrasonic nebulizers, operate on a variant of this process. The main component of an ultrasonic nebulizer is a piezoelectric transducer oscillating at ultrasonic frequencies. The energy generated by this transducer is applied to the sample which breaks down into small particles. The longitudinal wave propagated by the crystal produces a pressure that breaks the surface of the liquid-air interface into an aerosol. The efficiency of aerosol generation has been shown to be much greater than that of other nebulizers, in some cases, up to ten times better. Several advantages can immediately be deduced from this. More aerosol is produced and this is independent of the gas flow rate. Therefore, more analyte can be transported to the ICP torch at much lower gas flow rates [3]. This translates into longer residence times in the plasma and better sensitivity and detection limits. However, these advantages are lost with complicated matrices and other interferences such as spectral interferences and background shifts, can be enhanced as well. This method of nebulization can also result in greater memory effect [4].

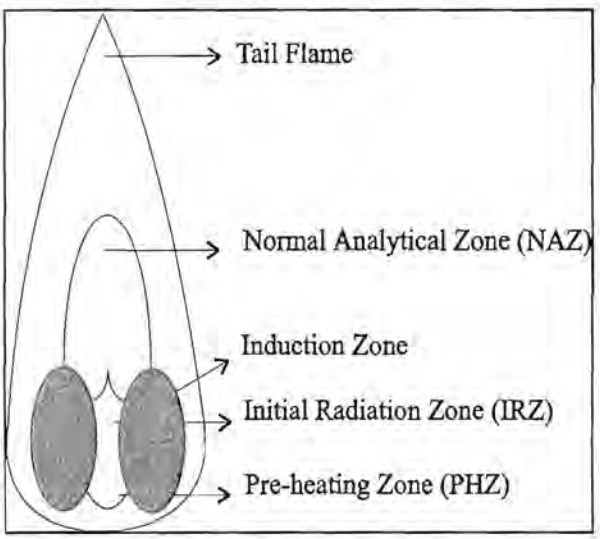
2.1.2 Plasma formation

Plasma formation occurs in a fused-silica torch. The torch consists of three concentric tubes, most often made of quartz, through which streams of Ar and aerosol flow. A plasma is a gas in which a significant number of atoms or molecules are ionised. Therefore, a magnetic field can be made to interact with the plasma. One of these interactions, the inductive coupling of a time-varying magnetic field with the plasma forms the basis of ICP-AES. The inductive coupling is analogous to the inductive heating of a metal cylinder [5]. Argon gas is ionised by a spark in the presence of the radio frequency (RF) field of the induction coil. As a result, some electrons in the spark gain enough energy to undergo inelastic collisions with Ar atoms. This collision may result in a transfer of energy from the electron to the Ar atom which ionises, releasing another electron which can in turn transfer energy from the coil to the gas. The magnetic field is generated by the high frequency currents flowing in the induction coil. The lines of force of the magnetic field are axially oriented inside the torch and follow elliptical paths outside the coil [1]. The electrons and positive Ar ions formed are both accelerated by the high frequency field of the coil. However, due to their far lesser mass, the electrons are accelerated to much higher velocities than the Ar ions, thus creating a domination in energy transfer by electrons. A steady-state plasma is obviously produced when the rate at which electrons are released by ionising collisions equals the rate at which they are lost by recombination processes. Ion-electron recombination in turn, emit light, producing a continuous spectrum corresponding to the distribution of ion kinetic energies in the plasma [1].

As the plasma thus achieved can obtain a gas temperature of between 5,000 to 10,000 K in the region of maximum eddy current flow, some form of thermal isolation must be provided to

protect the quartz torch. Reed's vortex stabilisation technique uses a tangential flow of Ar in the plasma. The flow of Ar cools the inside walls of the outermost quartz tubes and centres the plasma in the tube [6]. The position of the RF tube which generates the plasma is such that the plasma itself is anchored at the exit end of the concentric tube arrangement. The innermost tube is used to introduce the aerosol with Ar carrier gas to the centre of the plasma.

Figure 3: Zones in the ICP [1].



2.1.3 RF Generator

The RF generator therefore is required to supply an alternating current to the induction coil which is used to create and maintain the ICP's plasma. This current must have a selectable frequency as different samples call for various plasma states. There are again two main types of generators, "free-running" and "crystal controlled". The "crystal controlled" generator maintains a constant frequency regardless of the plasma impedance due to the presence of a piezoelectric crystal. This crystal usually operates in the low milliwatt output range as it cannot carry large currents. The high frequency modulation of the RF generator results in both high precision of analysis and enhanced signal to background ratio. By contrast, the "free-running"

generator allows the frequency of the oscillating current to vary according to the impedance of the plasma. The stability of the RF generator in both cases is ensured by water cooling [1].

2.1.4 Detection of emission

A photo multiplier tube (PMT) in the spectrometer is used to convert the light intensity into an electrical signal that can be quantified and therefore related to the concentration of the analyte in solution. As there are two main types of spectrometers available, two different set-ups are possible here. In the case of a simultaneous scanning ICP, an array of detectors is used to measure a number of lines at the same time, while a sequential ICP measures one spectral line after another by using a moving grating, giving an unrestricted choice of wavelengths. As discussed in chapter 1, simultaneous systems have a higher sample throughput as more elements can be analysed per time period. This is due to the fact that the wavelengths at which the elements are analysed are pre-selected in the manufacturing process. A direct result of this however is the lack of control over the analysis. Sequential systems have the advantage of flexibility of wavelength selection. This in effect, allows for variations in analyte concentrations and matrix types and the removal of interfering peaks by the selection of a different wavelength, with the major drawback of much longer analysis time [1].

2.2 Interferences in ICP-AES

There are several sources of error in ICP-AES. These can mainly be attributed to plasma affecting factors such as matrix effects, wing overlaps and chemical interferences. Matrix effects are usually less in ICP-AES than in flame or graphite furnaces. This is due to the environment of the plasma. Incomplete atomisation, especially of refractory species such as oxides, has plagued flame and graphite furnaces. Water and oxygen atom traces also cause incomplete

atomisation. In the plasma however, two factors minimise this type of matrix effect: an "inert" environment, as well as, high temperatures. Although the plasma is made up of mainly Ar gas, it is not totally inert. Water vapour from the sample and aerosol can produce a certain level of oxygen atoms within this plasma. the concentration of the oxygen atoms is similar to that in flames, approximately $2 * 10^{16}$ cm^{-3} [1].

2.2.1 Matrix Effects

Matrix effects however cannot be fully discounted. The very type of mineral acids or organic solvent used can play an important role in the emission signal. For instance, Cl from HCl has been shown [1] to weaken the signal from several elements such as Fe. While this can be in part compensated by the use of matched standards and blanks, this phenomenon cannot be completely removed. Organic solvents also play a major role in matrix effects [7]. As organic solvents are quite often made of large, complicated molecules, part of the energy normally used to excite atoms and ions is diverted to break down these molecules. This in effect results in a colder plasma and an entirely different emission spectrum. Organic solvents and very viscous solvents such as phosphoric acid, can also cause the plasma to extinguish itself due to high changes in electrical and thermal properties [8, 9]. Further problems are related to the vaporisation of the solvent. Not all solvents have the same viscosity which can result in different transport rates and nebulization rates as in the case of phosphoric acid. In many cases, excessive solvent loading of volatile solvents can be a problem. This can be circumvented by slower aspiration rates for readily nebulizable solvents. This can be shown by benzene, a very volatile solvent, where the maximum attainable aspiration rate is as low as 0.1 to 0.2 ml/min for an analytically useful plasma [8, 9]. This also ensures smaller primary droplets and increases the evaporation efficiency, allowing for a reduction in the nebulizer pressure [10-13].

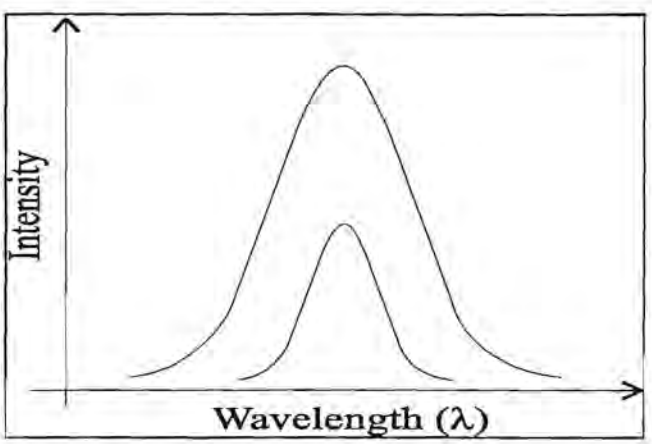
2.2.2 Spectral overlap

Spectral overlap, one of the biggest problems of ICP-AES, is a direct result of the high temperatures required to minimise vaporisation-type matrix effects and to maximise emission [14]. The usefulness of ICP-AES is directly derived from its ability to excite atoms to high energy levels thus, providing high signal-to-background (S/B) and signal-to-noise (S/N) ratios for many spectral lines. As many species are injected into the plasma which emit profusely, a high level of spectral interference can be expected. In the case of major elements this can be often discounted however, in the case of trace or weakly emitting elements, wavelength selection is necessarily dependant on other spectral features near that wavelength. Wavelength tables [15] have long been established with an average of 294 spectral lines being emitted per element with more than 100,000 wavelength lines being recorded in the 200-1000 nm range. This abundance of wavelengths can cause two types of spectral line overlap: Direct spectral overlap and Wing overlap.

2.2.2.1 Direct overlap

Direct spectral overlap occurs when two or more elements emit light at the same wavelength. In this case, no amount of increased resolution would achieve a separation of the two lines.

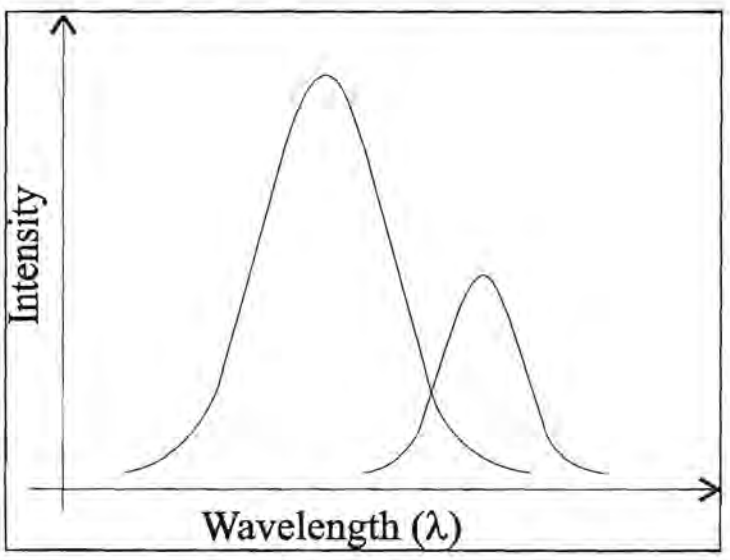
Figure 4: Direct Overlap [1, 16]



2.2.2.2 Wing overlap

Wing overlap occurs through Doppler broadening due to the high temperature of the instrument. In this case, several steps can be taken. Another line could be selected or better resolution could be sought. Inter-element correction is not recommended as small changes in the profile setting of the spectrometer can seriously alter the degree of overlap. Another source of wing broadening is resonance broadening. In this case, the width of the line profile can be said to broaden in proportion to the number of collisions between excited and ground state atoms. For example, the Ca I 393.37 nm and Ca II 396.85 nm lines, even at a concentration of 1 mg/ml can cause a non-linear elevation of the background as far as 10 nm away from the line centre. Therefore, a Ca matrix would severely interfere in the determination of Al at either the 394.4 or 396.2 nm lines.

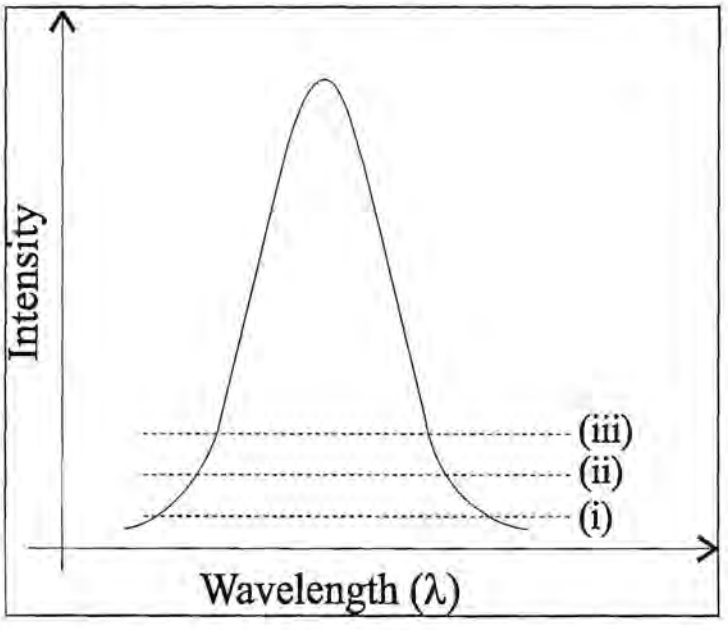
Figure 5: Wing Overlap [1, 16]



2.2.2.3 Continuum radiation

Another source of error in an ICP spectrum is continuum radiation. This radiation occurs from many sources such as electrons, Ar, and matrix species, both atomic and molecular As many operating parameters can affect the profile of the continuum radiation, several levels of background overlap can occur, as described in figure 6. Simple changes in operational parameters such as the Ar gas flow rate can severely alter the background radiation. A change in the matrix or recombination of ions such as Mg with free electrons can cause radiation over a wide range. These do not necessarily occur in the ground state and therefore cannot always be quantified. By using blanks, much of this background radiation can be mathematically removed. However, it is often necessary to use a dynamic background correction method in order to separate out this phenomenon.

Figure 6: Continuum Radiation [1, 16]



2.2.3 Stray light

Stray light should always be considered when using a spectrometer. Stray light is defined as light which reaches the detector unintentionally. There are several sources, mainly occurring from defects in the grating, for stray light such as line "ghosts" from periodic errors in the grating spacing; satellites, near scatter, or "grass" resulting for regular or irregular grating defects; or far scatter which occurs several bandpass away from an affected line, generated by a localised roughness in the groove shape. As with all man-made instruments, dispersive devices are not perfectly made, which results in instrumental beam aberrations. This problem is carried over to other monochromator devices such as slits, slit mechanisms or simply optical misalignment. Particles in the optical path, degradation of anti-reflection coatings on optics can also cause stray light. Several methods to minimise stray light interferences have been devised. These include solar blind PMT which will not respond to radiation above 350 nm, double monochromators, as well as, correction coefficients and linear scanning across the analyte line to provide dynamic correction.

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CHAPTER 3

ION EXCHANGE

3.1 Introduction

Ion exchange is a fairly new technique in chemistry. This natural phenomenon has come to the fore of research in the past 50 years as indicated by scientific publications [1]. This technique, while on the surface fairly simple, has become a very useful tool for speciation and extraction. Over the last half century this method has been extensively developed, mainly in the purification and demineralisation of water. One of the earliest records of ion exchange comes from Aristotle who found that sea water loses some of its salt content by filtration through certain types of sand [1,2]. This phenomenon was then largely left alone until recently when the first synthetic, industrial ion exchanger was developed by Horm and Rümpler [1]. This development, among others, sparked research into new resins that had superior chemical stability at both low and high pH values, and better properties than the inorganic ion exchangers used at the time. In 1935 Adams and Holmes were able to synthesise the first organic ion exchange resins [1].

The principle of ion exchange as mentioned before is fairly simple. Ion exchange is the reversible exchange of ions between a solid matrix such as the ion exchanger and a solution. Ion exchanger must therefore be insoluble, solid material with ionogenic groups. Ionogenic groups are charged centres to which anions or cations can bond. Through an electrolyte solution, these counter ions can then be stoichiometrically exchanged for equivalent amounts of similarly charged ions [1,3]. This phenomenon has proven to be highly useful in the recovery of metals from industrial wastes and the

separation of rare earth metals. Within a chemical laboratory context, ion exchangers have proven to be highly useful in a variety of sample preparation and manipulation procedures. These include the removal of interferents from samples, and pre-concentration of trace levels of metals as well as the separation or speciation of equivalent species from samples. In this work, the main use of ion exchangers was the last one, namely the speciation of As and less important, the removal of other ions present in the sample.

3.2 Ion Exchange Resins

Although several different substances exhibit some ability to act as ion exchangers, synthetic organic resins have become the major players in this field. This prominence is largely due to the ability of synthetic chemists to generate fairly ion specific resins [1,3]. These resins consist of a 3-dimensional network of organic polymers such as styrene-divinyl benzene, to which ionic groups such as NR_3^+ are chemically bonded. In essence these groups are the ionogenic groups of the ion exchanger. The major drawback of these groups is the hydrophilic character which the polymers adopt which then allows them to dissolve in aqueous solutions. To prevent this, a cross linking compound such as divinyl benzene is introduced during the polymerisation of the resins in order to interconnect the hydrocarbon chains. Through this simple chemical process, the polymer's molecular weight and mechanical stability can be dramatically increased while its solubility decreases. This high level of cross linking however does have two side effects which may not always be beneficial. Primarily, the cross linking will prevent the resin from extensive swelling in solutions. This in turn inhibits the mobility of counter

ions and therefore lowers the exchange rates. From the name of the resin, eg. Dowex 1X8 resin, we can tell the percentage of cross linking (8% in this case).

Synthetic resins as mentioned before have become the preferred ion exchange medium. This is due to the fact that the ion exchange behaviour of the resin is a direct result of the number and nature of the fixed ionogenic groups. The number of groups fixes the capacity of the resin while the nature of these groups affects the exchange equilibria. These resins tend to be pH dependent as the functional groups are often acidic or basic in nature. This means that they will tend to be more readily ionized at certain pK_a (or pK_b). For instance, when the pH is lower than the pK_a of an acid functional group as is the case for NR_3-type functional groups, then the ionogenic groups will not be ionized and no ion exchange will be possible. It is therefore critical that the proper conditions are used to allow the maximum potential of these resins [1].

The resins are often divided into three major categories, based on their ionogenic groups. These are: Anion, Cation, and Chelating ion exchange resins.

3.2.1 Anion Exchange Resins

When the fixed ionogenic groups have positive charges (or are basic groups), the resin is classified as an Anion Exchange Resin. These tend to have quaternary ammonium functional groups as their ionogenic centres [3]. By varying the degree of substitution of these terminal amine groups, it is possible to engineer strong, medium and weak base anion exchange resins with highly different pK_b.

Strong anion exchange resins contain highly substituted ionogenic groups such as

trimethylamine, which ionizes at pH values from 1 to 15 [2]. These resins will deteriorate at temperatures above 60°C, but will withstand most common solvents as well as certain oxidising agents. Weak anion exchange resins are typically lower substituted ammines or ammonia, eg. NH_2R^+ and NH_3^+ which are only protonated below a pH value below 9. The third class of anion exchange resins, medium anion exchange resins, falls between these two and contain both strong and weak base functional groups and will not therefore withstand high pH values.

3.2.2 Cation Exchange Resins

In this case, the counter ions are bonded to negatively charged ionogenic groups in the resin. These are the opposites to anion exchange resins in that the functional groups are acidic in nature with varying strength. There are also three main classes of Cation Exchange Resins, strong, medium and weak, based on their pK_a values.

Sulphonic functional groups (SO_3^-) form the basis of the most common strong acid cation exchange resins. These are typically bonded to benzene rings within the organic polymer matrix. The pK_a of these groups is approximately equal to one and therefore they will be ionized by the presence of a strong acid [2]. Weaker acid groups such as $PO(OH)_2$ or $OPO(OH)_2$ are the typical ionogenic groups of medium cation exchange resins. As these groups are not found dissociated at low pH values, the minimum pH at which these are useful is 5. Weak cation exchange resins are made up of carboxylic acid functional groups as a rule. These are very pH dependent and are used at a pH of between 6 and 14.

3.2.3 Chelating Ion Exchange Resins

This class of resins are probably the most selective. The functional group is, in this case, a chelating agent which will interact with a limited number or metal ions [3]. Therefore, by carefully selecting the chelating agent, the resin's affinity for certain metal ions can

easily be designed while the size, charge and other physical characteristics of the metal ions and resin will be of secondary importance. By careful pH control, the selectivity of this resin can be further enhanced. Trace element concentration and separation of certain elements is enhanced in this method as the metals are chemically bonded to the resin. However, as the exchange rates are determined by either secondary chemical reactions or particle diffusion [2], the kinetics of the exchange reactions are unfavourable.

3.2.4 Capacity

Each resin has a specific capacity which is best defined as the number of ionogenic groups contained by 1 g of the dry resin [1,3,4]. Resins with higher capacity will therefore accommodate more ions though the trade off is more difficult elution and therefore will require higher eluent concentrations to effect complete elution. Low capacity resins are generally preferred in ion chromatography as the separation of ions should be achieved quickly and with low eluent concentrations.

3.2.5 Selectivity

3.2.5.1 Selectivity coefficient

Ion exchange, like many other reversible chemical reactions can be expressed as a general equilibrium reaction:

$$a\,A_s + b\,B_r \rightleftharpoons a\,A_r + b\,B_s \qquad (1)$$

Where a and b represent the molar quantities of exchanged ions A and B respectively. Subscripts r and s represent the phase of the ion, r for the resin phase while s stands for solution. The equilibrium constant for the reaction can then be represented as:

$$K_B^A = \frac{[A_r]^a * [B_s]^b}{[A_s]^a * [B_r]^b} \qquad (2)$$

Where $[A_r]$ and $[B_s]$ are the concentrations of ions A and B in the resin and solution phases respectively. Normally a and b are expressed in terms of mmol / l for solutions and mmol / g for resins when a and b are not equal. [5] From the affinity of ion exchangers for certain species, it is possible to deduce that the equilibrium constant will not equal one. From this, it is possible to infer a selectivity coefficient indicating the specific affinity of a resin for an ion. Therefore, should the selectivity constant K_B^A be greater than one, then the resin can be said to have a higher affinity for ion A than for ion B. This selectivity coefficient can also be used to determine whether ions would be useful as eluents eg. ions (A) with high K_B^A values are often good eluents.

3.2.5.2 Factors influencing selectivity

Many factors can influence the selectivity of a resin. Some of these have been referred to previously such as the nature of the resin as well as the type and concentration of the ions in solution. The exchange of ions on the resin typically involves the formation of chemical bonds between ions in the solution and the ionogenic groups of the resin. The affinity of the resin for certain ions is directly related to the interaction between the ions and the ionic groups or the matrix. The stronger this interaction when these bonds are formed, the higher the affinity of the resin.

At the same time, ion exchange can also be due to purely electrostatic interactions instead of chemical bond formation. As electrostatic interactions can be proven to be

proportional to the charge of the ion while being inversely proportional to the distance between the charges, ion exchange resins will have a preference for ions of higher valencies as well as ions with smaller, solvated equivalent volumes and a greater polarizability. Due to this effect, the ions tend to be localized in the neighbourhood of the fixed ionic groups.

Selectivity can be decreased through secondary reactions such as complex formation. However, should cations form anionic complexes with ligands in solution, anion exchangers tend to prefer the anion which will form the stronger complex or the complex with the greater average ligand number [3].

By decreasing either the temperature or the solution concentration as well as increasing the degree of cross linking, the selectivity of a specific resin may be increased [1].

3.2.6 Distribution coefficient

The distribution coefficient, like K_B^A is a measure of the affinity of a resin for a particular solute ion A and is defined as below:

$$D_g = [A_r] / [A_g] \qquad (3)$$

As previously, $[A_r]$ and $[A_s]$ are the concentrations of the exchanged ion A in the resin (mmol/g) and in the solution (mmol/l) respectively. Therefore, a large distribution coefficient would signify a greater affinity of the ion for the resin than for the solution. This value, D_g, however is specific for the ion exchange resin and the eluent conditions used. This value also tends to increase with increasing atomic weight. [3]

3.2.7 Kinetics of Ion Exchange

An exchange resin's usefulness in either separation or concentration processes is often determined by the rate at which ion exchange occurs. As the ion exchange process is basically a diffusion process, the following equation can be used to represent the overall process:

$$A_s + B_r \rightleftharpoons A_r + B_s \qquad (4)$$

The simpleness of this equation belies the fact that the process often involves five distinct reactions occurring simultaneously. Three further steps can be used to describe this reaction based on the electroneutrality principle, which require that the flux of ions A and B are equal: [5]

(i) The diffusion of ions A from the solution to the surface of the resin particle occurs while ion B diffuses from the resin surface into the external solution.

(ii) Ion A diffuses from the resin surface to the ion exchange position in the particle while ion B diffuses from the ion exchange position to the surface of the resin.

(iii) Ion B and ion A are exchanged at the exchange position.

From any of these reactions, the ion exchange rate can be extrapolated [1,5]. Generally, reaction (iii) is not considered to be the rate-determining reaction as reactions of free dissociated ions in aqueous solutions are very fast [5]. In the case of chelating ion exchange resins, this rule does not usually apply as complexing reactions are very slow[1] and therefore, the chemical exchange of the ions will then be the rate-determining reaction.

This in effect leaves us with two reactions, (i) and (ii) from which the ion exchange rate can be determined. These two reactions are diffusion processes. In reaction (i), the diffusion rates of ions A and B will be primarily determined by the degree to which the solution is agitated. Under normal condition, the solution is well agitated in both batch and column processes. Hydrodynamic factors, however, indicate that a thin film of solution which directly surrounds the resin particle will be static, eg no agitation will occur in this film. The name of this film, the Nernst film or the Nernst diffusion layer (δ) is a tribute to Nernst who developed the concept. This thin film then can be considered to be the limiting factor for the diffusion of the ions A and B. As these ions are well mixed in the bulk of the solution, the rate of diffusion of the ions depends on the film diffusion rate.[1]

Ion exchange resins with low degrees of cross linking, small particle sizes, and insufficiently mixed, dilute solutions are especially affected by film diffusion. The overall reaction rate can be increased as follows in these cases:[5]

- The Nernst film may be decreased through increased agitation of the solution in batch processes, or increased flow rates in column processes.

- The concentration of exchangeable species can be increased.

- Smaller resin particles will result in an increased surface area of the ion exchange resin.
- Higher temperature should increase the diffusion rates.

Should reaction (ii) be the rate determining step, then *particle diffusion* is involved. This means that the diffusion of the ions within the particle becomes more important[5]. Generally, this indicates that the resins used have a high degree of cross linking and are made up of large resin particles. The diffusion rate can be increased through the use of smaller resin particles, higher reaction temperatures, higher capacity resins, as well as through the use of a resin with a lower degree of cross linking which will result in an increase in the porosity of the resin particles [2,5].

When solutions have a concentration of 0.001 mol/l and lower then, film diffusion is the rate determining step. For solutions with concentrations near 0.01 mol/l, particle diffusion starts to play a bigger role and at 0.1 mol/l or higher, particle diffusion becomes the rate determining step.

As increasing the reaction temperature and using smaller particles will increase the reaction rates of both film and particle diffusion, the overall ion exchange reaction rate can be increased without first determining which of these two processes is rate determining.

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Chapter 4

Comparison of a Micro-concentric nebulizer with a Meinhard nebulizer

4.1 Introduction to nebulizers

As with many emission and absorption techniques, ICP-AES relies heavily on the sample introduction efficiency. Most analytical samples do not conform in size, concentration, viscosity or even phase. The sheer array of sample types makes it difficult to standardize sample introduction methods. However, some specialised equipment has been developed for the ICP-AES to facilitate this process. In the case of solutions, the sample introduction of choice is a nebulizer. These involve several categories such as, pneumatic nebulizers and ultrasonic nebulizers.

Research into nebulizer design and performance, the effects of spray-chamber design, factors influencing droplet size, formation, and distribution, and methods for the characterization of nebulizers has intensified, as demonstrated by the increased volume of papers published.

4.2 Theory of nebulizers

4.2.1 Pneumatic nebulizers

The most widely used solution sample introduction method is Pneumatic nebulization. The efficient generation of aerosol with a small average droplet size requires a high gas velocity in the nebulizer. To generate a flowrate of aerosol carrier gas of about 1 l/min, a nebulizer must have very small orifices, typically 200 μm for the gas and the liquid flows. This means that the manufacture and alignment of these nebulizers can be quite difficult. The main disadvantages of these nebulizers is the ease with which they can be blocked. Fine

suspended matter present in the solution or even fibres introduced when the tubing is cleaned before each sample introduction can result in the blockage of these orifices. Should the solution analysed have a high salt content, then the salt tends to precipitate out at the tips of the nebulizer, leading to partial or complete blockage. This effect, the "salting out" effect occurs most commonly around the annular gas aperture of concentric nebulizers. By using a humidified argon gas flow (a 'gas-wetter'), this problem can be alleviated somewhat or alternatively, the tip of the nebulizer can be washed between sample aspirations (a 'tip-washer').[1]

The most common pneumatic nebulizers are:[1]

- concentric nebulizer, e.g. the Meinhard nebulizer
- cross-flow nebulizer
- Babington-type nebulizer
- glass-frit nebulizer
- grid nebulizer
- jet-impact nebulizer

4.2.1.1 Concentric nebulizers

The concentric design offers a greater mechanical stability than the adjustable cross-flow designs at the cost of more blockage. Both the concentric and cross-flow designs make use of the Venturi effect, using the reduced pressure resulting from a fast moving gas jet to cause the solution to be drawn into this gas jet and to be broken into droplets of various sizes. Because of the Venturi effect, concentric and cross-flow nebulizers are generally self-feeding, removing the need to pump the sample. However, in the case of samples with

differing viscosities, the feed rates will differ and a peristaltic pump should be used to minimize these differences.[2]

After primary nebulization, a spray chamber is used to filter out the larger droplets, and the finer droplets pass on into the excitation source. Some designs use an impact band immediately in front of the jet for the secondary nebulization of the larger droplets.

The finer details of these nebulizers such as the alignment of the gas and solution tubes and overall geometry depends on the manufacturers. Some designs have a fixed geometry while others allow the alignment of the gas and solution tubes to be adjusted by the user. Several designs are currently in use though the Meinhard type C nebulizer is reported to be more tolerant of high-solids sample solutions than types A and B.

4.2.1.2 Cross-flow nebulizers

Though the cross-flow design is much more tolerant of solutions with high salt contents than the concentric design, both systems are subject to periodic blockages by stary particulate matter, and to salting out, which is often caused by the reduction in temperature that accompanies the Venturi effect. Problems associated with salting out tend to occur in solutions in which the total salt content is greater than 1 percent. The cross-flow nebulizer, as its name indicates, relies on the gas flow and the sample solution flow coming at 90 degrees to each other. The gas flow is typically delivered at a horizontal position with the solution coming vertically up a capillary. The fast moving aerosol gas jet causes the droplets formed at the top of the solution capillary to from a spray which can then be passed through a spray chamber.[1]

Here again, the overall design can vary as the capillaries can either be fixed in position by the manufacturer to allow greater stability and reproducibility or, they can be adjusted by the user to allow for better nebulization of different solutions.

4.2.1.3 Babington-type nebulizers

Due to the design of these nebulizers, this particular model is commonly used for solutions with high salt content, such as 10 percent sodium or more, and slurries of solid powders. The original design involved the solution being poured over a hollow sphere with a hole in it through which the nebulizing gas issued in a jet. Since then the design has undergone many modifications. The modern Babington-type nebulizer has the sample solution or slurry trickling down along a 'V'-shaped groove. The sample is fed into the V-groove by a peristaltic pump. A gas jet which issues from a capillary hole in the middle of this groove, disrupts the solution flow and causes nebulization. This design has the major advantage that it is virtually unblockable in routine analytical work. Another advantage is that Babington-type nebulizers which match the performance of commercial nebulizers can be constructed in the laboratory from simple materials.[1]

4.2.2 Ultrasonic nebulizers

Ultrasonic nebulizers are somewhat less common than pneumatic nebulizers even though their sensitivity has been reported as being up to 4 times higher. This is higher sensitivity is mainly due to the proportion of small particles (less than 10 μm) generated in the aerosol which is higher than that produced by pneumatic nebulizers. The sample solution is pumped onto a vibrating crystal transducer (1 to 10 MHz) which generates the aerosol.[3]

One of the major drawbacks of this type of nebulizer is that often a desolvation step is required to reduce the water loading in the aerosol and therefore keep the plasma ignited. This means that a desolvation apparatus (heater and condenser) has to be used which increases the path followed by the aerosol and increases the analysis time as well as the memory effects. The increased memory effects in turn require longer wash-out times which again lengthens the analysis time. Ultrasonic nebulizers also suffer from poor long-term stability, and their performance is sensitive to small changes in the operating parameters.

However there are several benefits to using this type of nebulizer. With or without desolvation, ultrasonic nebulizers can give detection limits that are an order of magnitude or more lower than those normally obtained by ICP-AES. With a desolvation system, Taylor and Floyd have reported detection limits that were 5 to 10 times lower for 31 elements while Fassel and Bear report that on a continuous-flow nebulizer with a desolvation system the detection power was improved by five- to fifty-fold.[1]

The principal cause for improvement of detection limits and signal to noise ratio is in most cases an improvement of the droplet size generated by the nebulizer. Smaller droplets lead to lower background emission with, at the same time a slight drop in signal intensity due to lower analyte levels. Further improvements can be derived from an overall raising of the plasma temperature as the plasma solvent loading is reduced. This means that less of the energy contained within the plasma is diverted to breakdown the matrix. Not only does the droplet size play an important role in the signal to noise ratio, but the exact size distribution has a major impact too. With smaller droplets comes usually lower droplet weights. This translates into more of the analyte being transported, through the spray chamber where the

heavier droplets are removed, to the plasma. In other words, as the spray chamber tends to let a range of droplets through, the ideal nebulizer would have a Gaussian particle size distribution to match the spray chamber's operating range. Should a nebulizer produce only some low mass or diameter droplets, with the majority being heavy droplets, that nebulizer would be wasting most of the solution. Ideal nebulizers would therefore be those which allow the introduction of a "dry" analyte as opposed to those used currently which depend on the creation of an aerosol [1].

Nukiyama and Tanasawa [4] developed an equation describing the particle size distribution for concentric nebulizers:

$$d_0 = 585\left[\frac{\sigma^{0.5}}{c\rho^{0.5}}\right] + 597\left[\frac{\mu}{(\rho\sigma)^{0.5}}\right]^{0.45}\left[1000\frac{Q_l}{Q_g}\right]^{1.5} \qquad (5)$$

where ρ is the density (g/cm^3), σ is the surface tension (dynes/cm), μ is the coefficient of viscosity (dynes/cm^2), c is the relative velocity between the gas and the liquid (c_g-c_l)(m/s), and Q_l and Q_g are the volume flows of the liquid and gas, respectively. By playing with these parameters, one at a time, optimal operating parameters can be found for each nebulizer.

4.3 Experimental for the particle size distribution:

The μ-Laser Particle Analyser (μ-LPA) was mounted on a stable base (see appendix). A holder for the nebulizer was placed on a screw next to a ruler which allows us to determine the distance from the nebulizer tip to the cell of the μ-LPA, see diagram. Several sleeves were designed to allow the various nebulizers to fit into the holder. A 0.5 mm i.d. tube was used across the peristaltic pump with a 0.4 μm i.d. tube making the connection to the

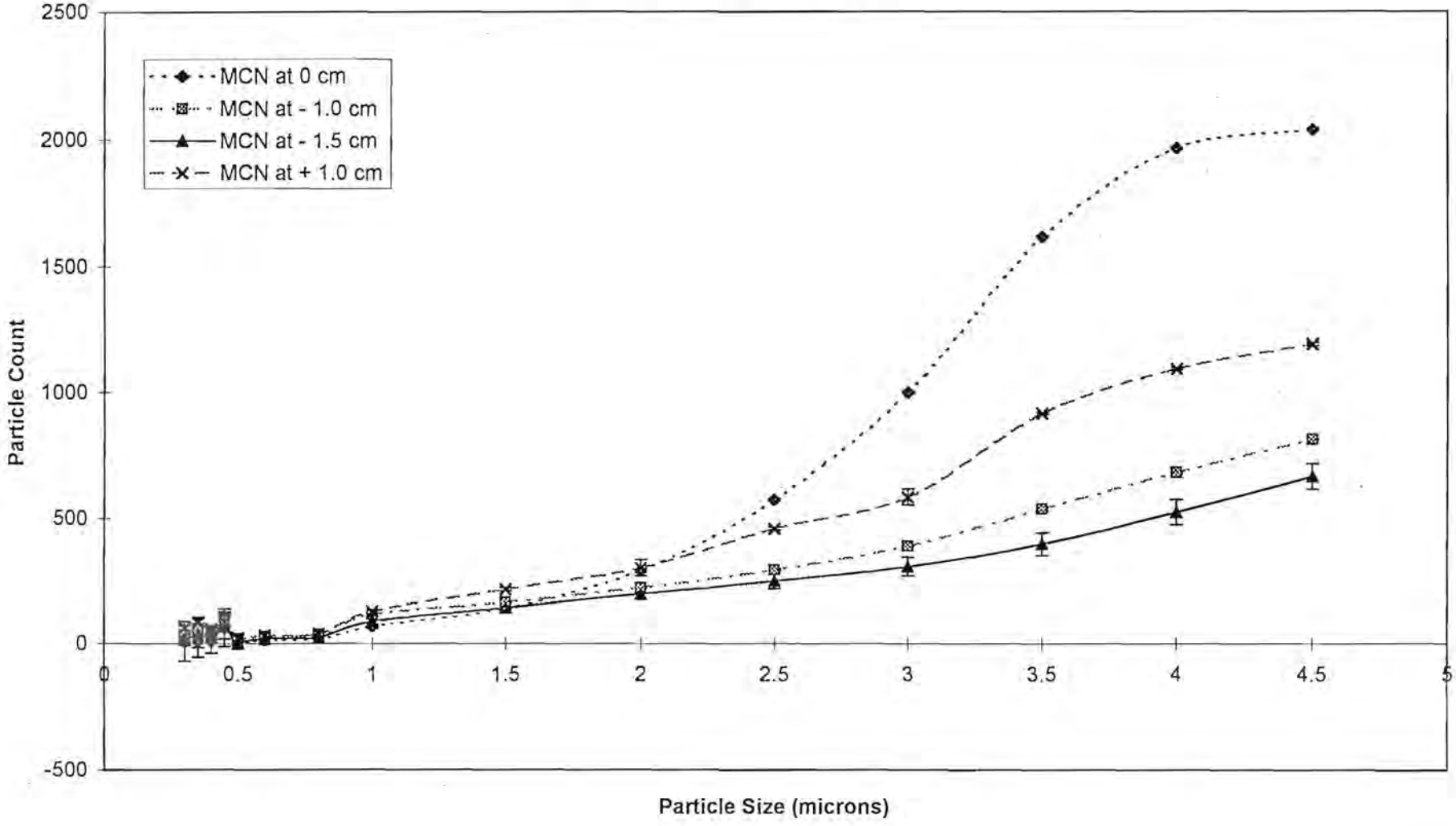
nebulizer. In the case of the Micro-Concentric Nebulizer (MCN) the size of this tubing was of particular importance as the inner diameter of the MCN is 0.2 μm and therefore the MCN can get easily blocked by particulates in the solution. Special glassware was also designed (see appendix) for use with the MCN to minimize contamination and filter out particles larger than 0.45 μm. The pump speed was varied from 200 rpm to 900 rpm, the Ar pressure from 40 kPa to 200 kPa and the distance from the nebulizer tip to the μ-LPA from -1.0 cm (nebulizer tip inside the cell) to 2.0 cm. Four nebulizers were considered: MCN, Meinhard type 'C', V-Groove and Cross-Flow. The effect of a surfactant with the MCN and Meinhard nebulizers was also explored. The resulting data was plotted as number of particles vs particle diameter size. This allowed us to explore the effect of changing each parameter of the Nukiyama and Tanasawa equation in turn.

Results and Discussion:

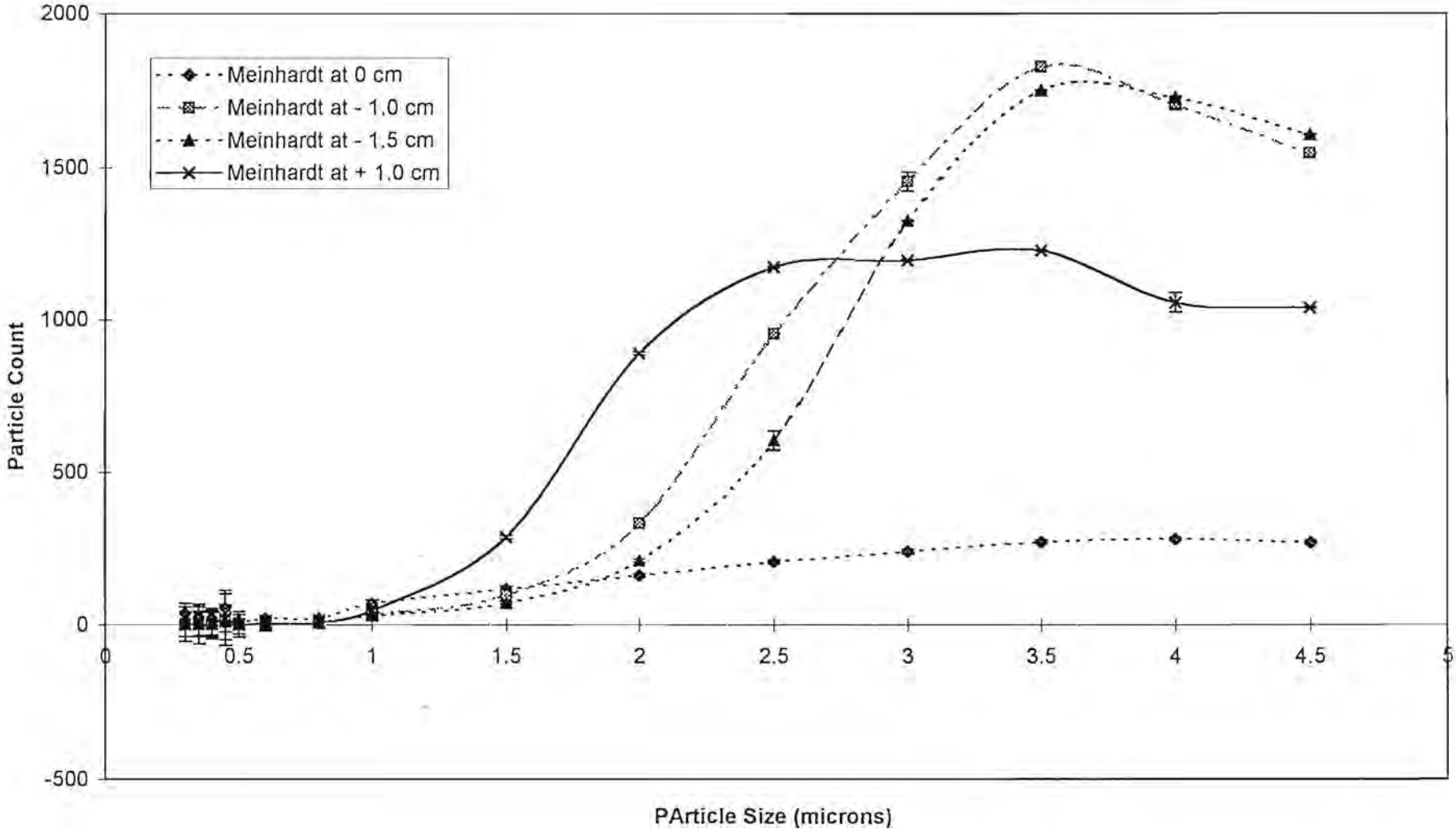
Most of the graphs appear to have two common features. These are the initial peak ca. 0.45 μm and a secondary peak starting near 1 μm. For this reason most nebulizers operate with a spray chamber which removes the larger droplets from the aerosol. The Cross-flow and V-Groove nebulizers seem to follow the same trend although in most cases the initial peak may have started well below the detection limit of the μ-LPA, as can be seen from the decreasing shoulder at the beginning of the graph. The V-Groove's secondary peak is also found at a much lower diameter range, between 0.5 μm and 1.0 μm.

When comparing graphs 1-4, it can be seen that the particle count under these conditions is greatest for the MCN and smallest for the V-Groove. This can be attributed to the fact that the flow rate delivered by the tubing is optimal for the MCN and probably insufficient for

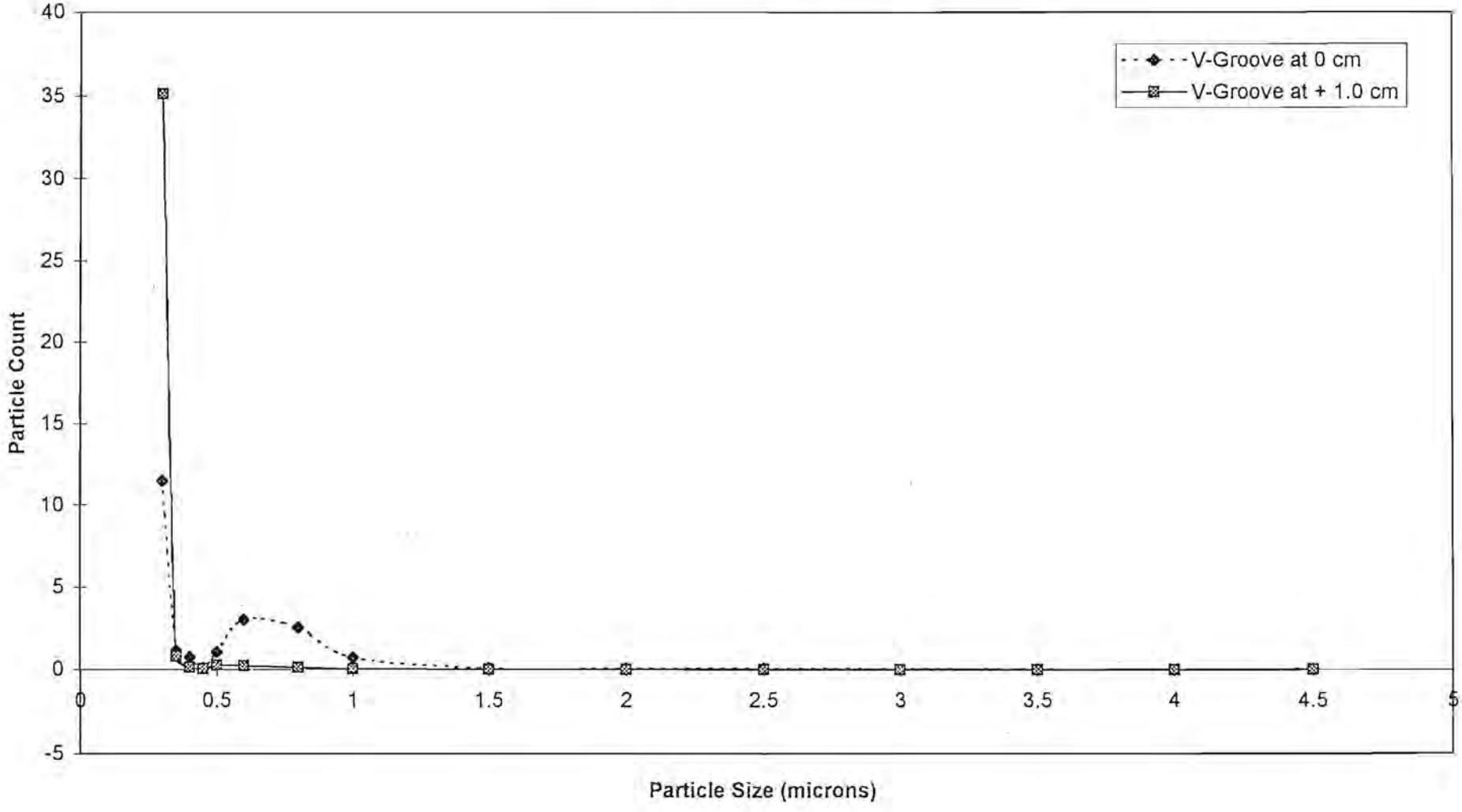
Graph 1:
MCN at different positions



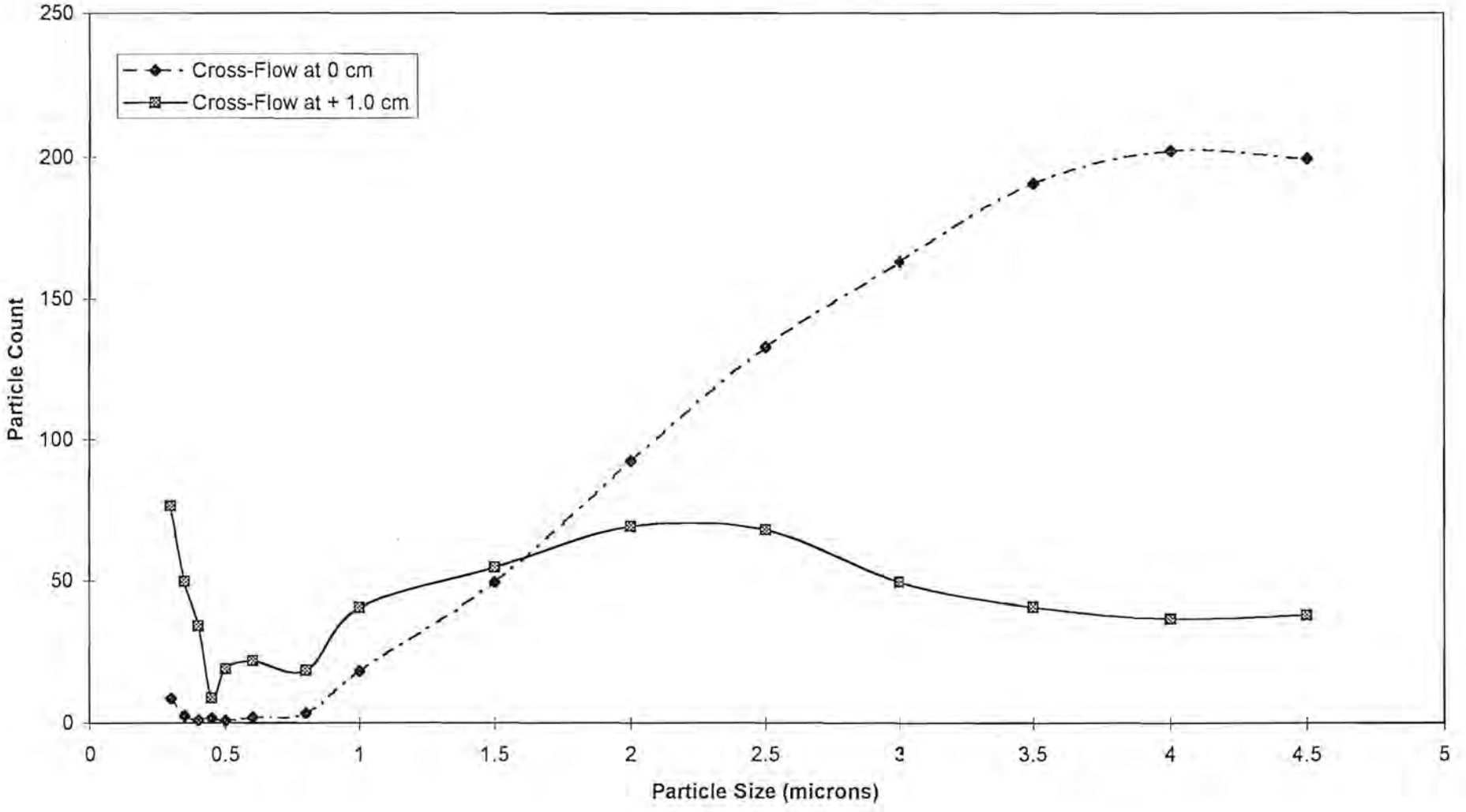
Graph 2:
Meinhardt at different positions



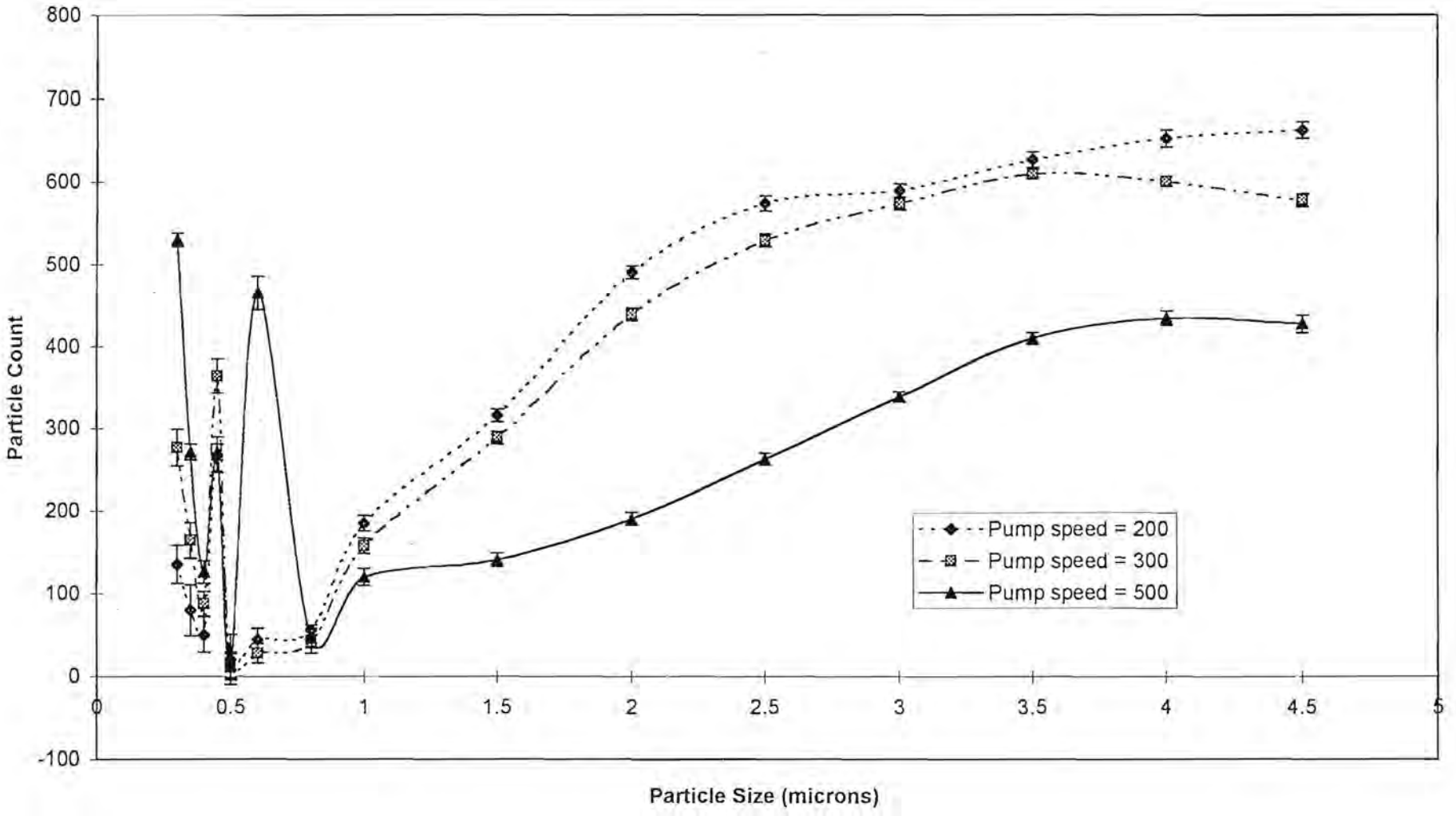
Graph 3:
V-Groove at different positions



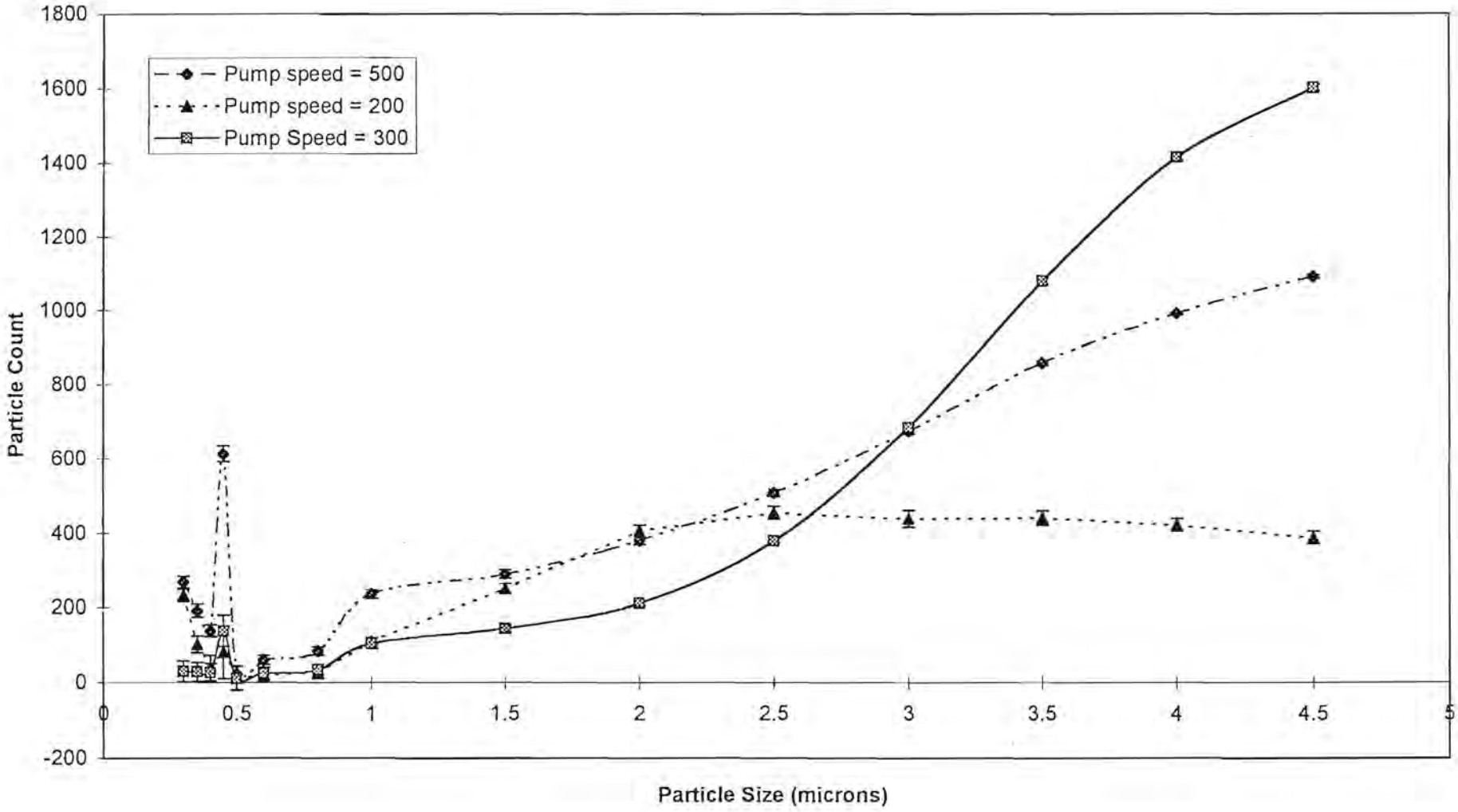
Graph 4:
Cross-Flow at different positions



Graph 5:
MCN at Ar = 100 kPa



Graph 6:
MCN at Ar = 140 kPa



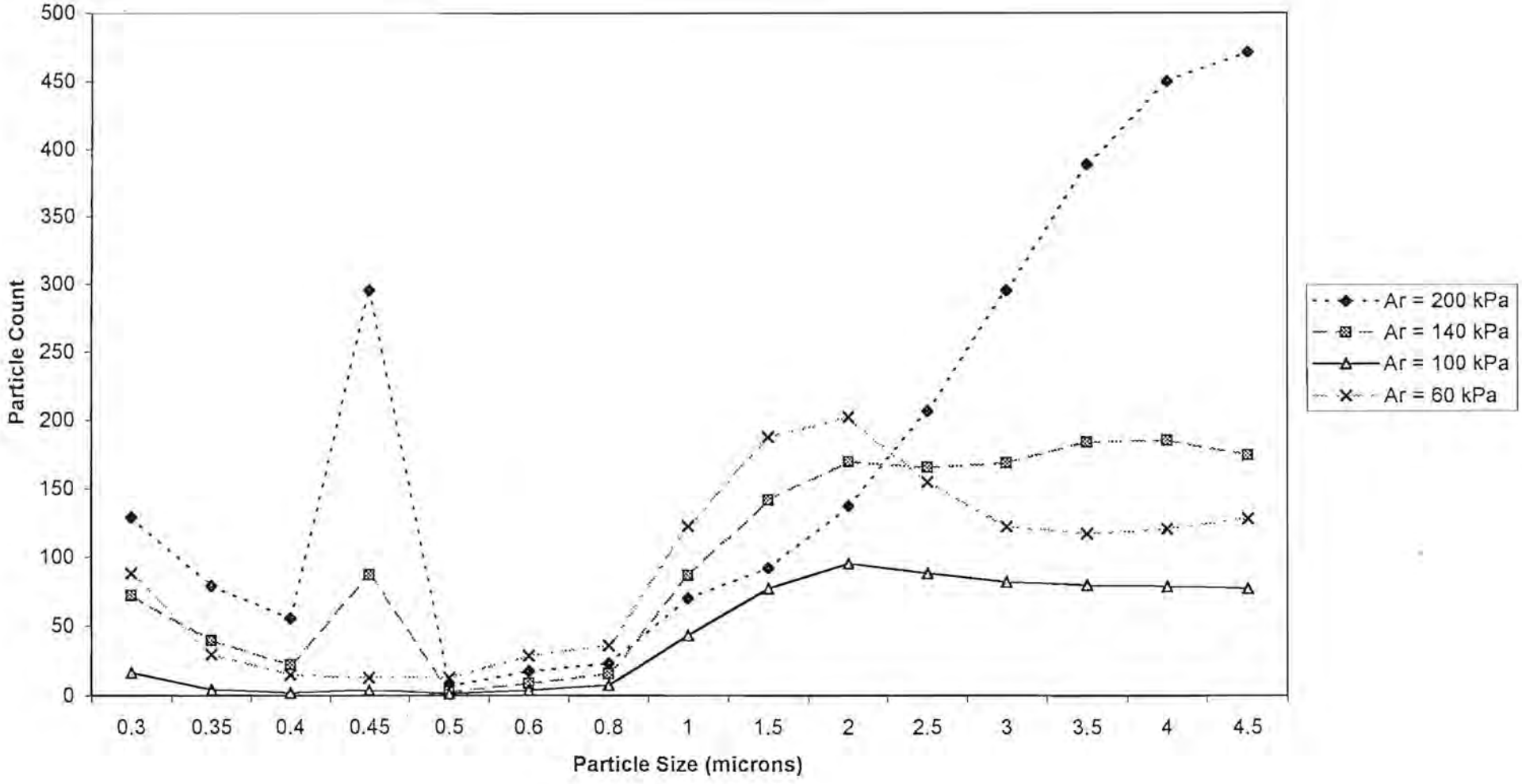
the V-Groove and the Cross-flow. By using a μ-LPA which could go lower than the 0.3 μm limit imposed by the current instrument, this premise could be fully explored.

Increasing the pump speed at lower pressures such as 100 kPa changes the position of the initial peak. Higher flow rates cause greater particle diameters as can be seen most easily on graph 5. However, at the higher pressures this effect is no longer evident. Graphs 4 and 6 illustrate the relationship between the Ar pressure and the flow rate. At lower pressures, lower flow rates are required in order to maintain the initial peak while at higher pressures, the higher flow rates generate larger initial peaks.

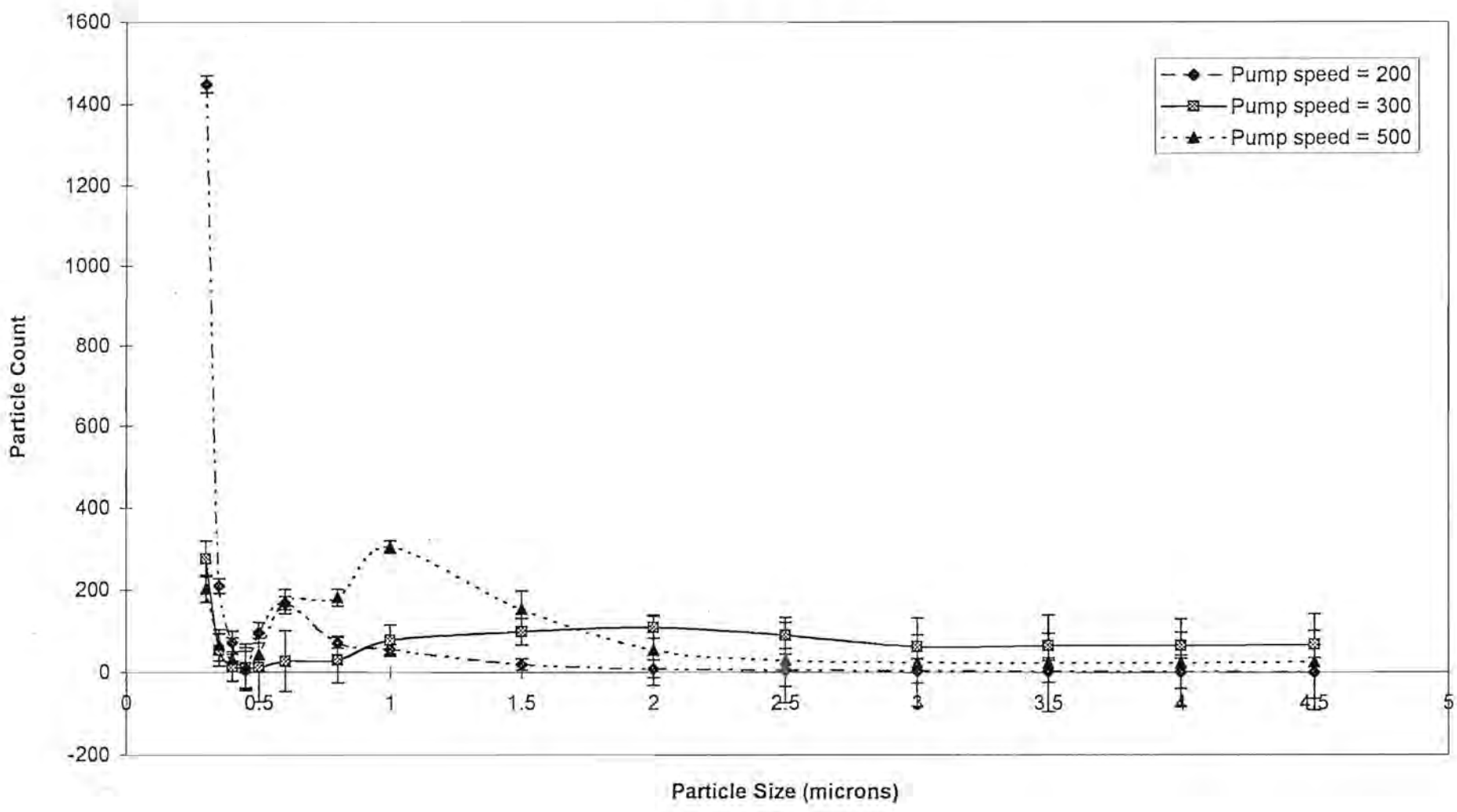
The MCN nebulization process is most efficient at approximately 100 kPa Ar for a pump speed of 500 rpm (graph 7) while the Meinhard nebulizer appears to have its highest efficiency at 200 kPa for the same pump speed (graph 4). The V-Groove and Cross-Flow nebulizers were disappointing in this respect as they did not produce any large level of particles.

When the % RSD is compared for all these nebulizers, the trend indicated from graphs 8-12 is that the MCN produces the most even spray while the Cross-flow has the largest standard deviation in aerosol size. The Meinhard nebulizer produces in most cases a very constant spray although its %RSD is slightly larger than the MCN. The inhomogeniety of the sprays, especially for the MCN can be attributed to the pump. Indeed when the spray is examined closely, it is possible to see it pulsating at the speed of the peristaltic pump. While this phenomenon is more difficult to observe with the Meinhard nebulizer, the trend still exists. It was not possible to determine this trend visually for the Cross-flow or V-Groove nebulizers.

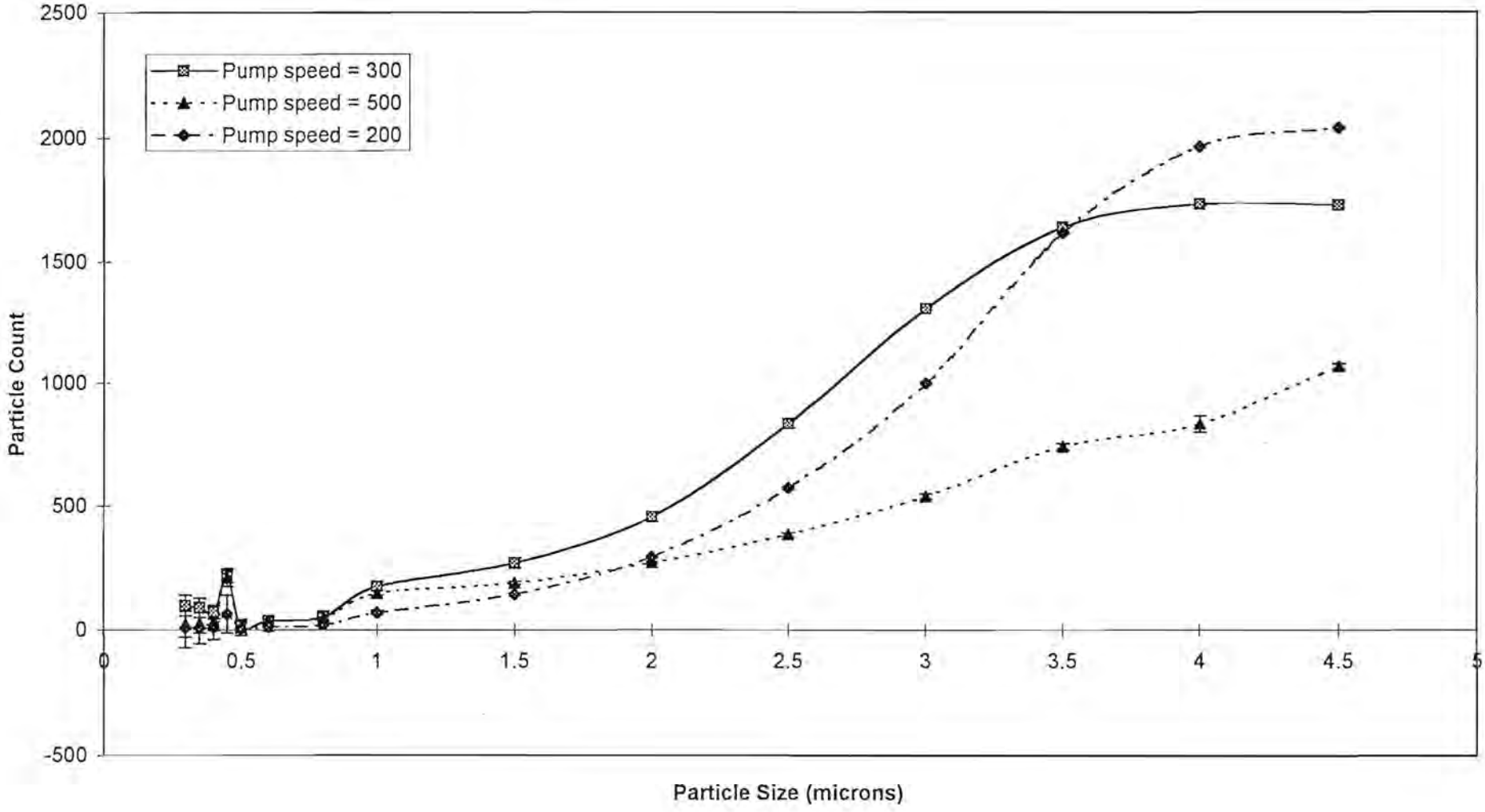
Graph 7:
Meinhard at pump = 500 RPM



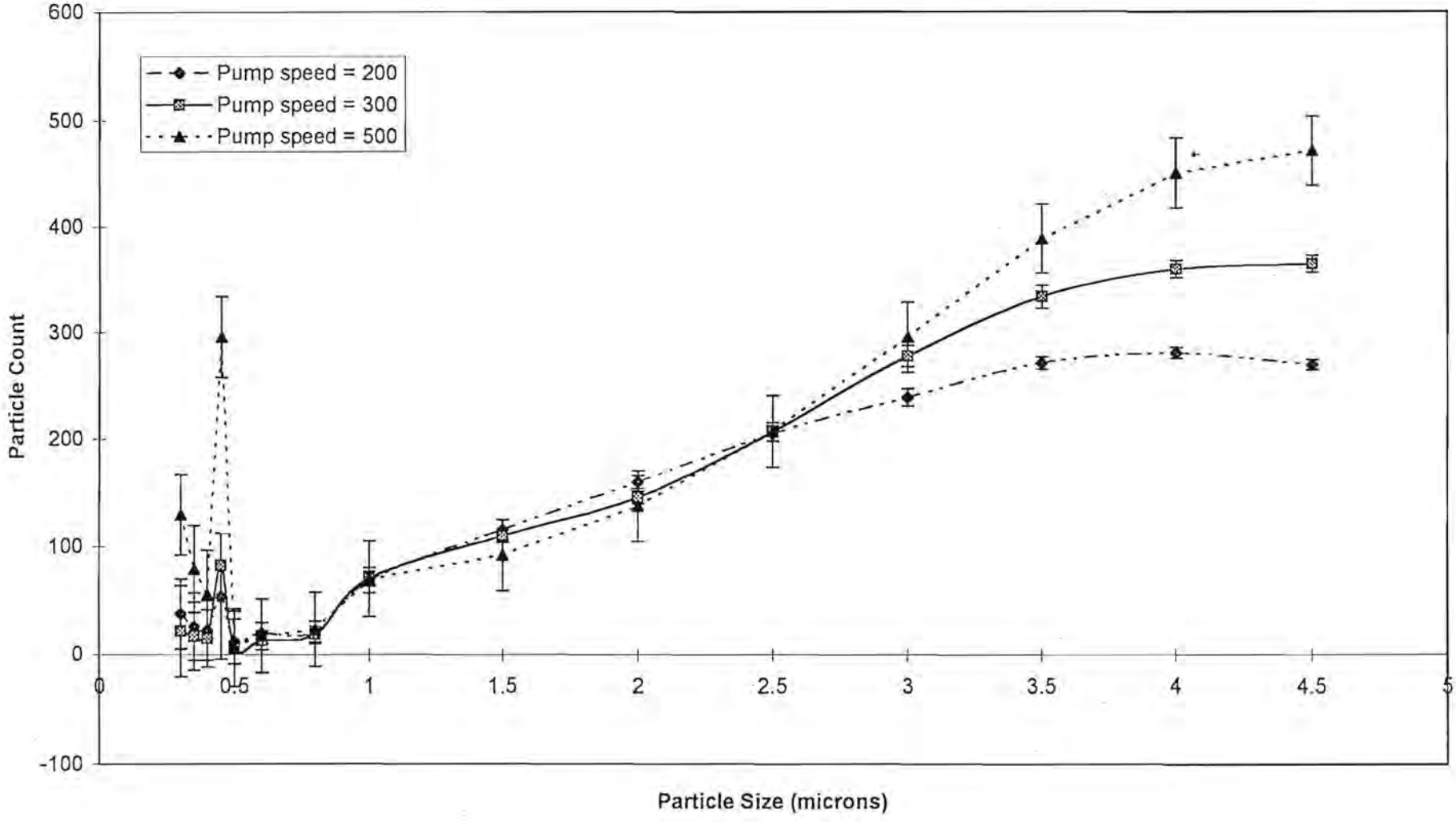
Graph 8:
MCN at Ar = 60 kPa



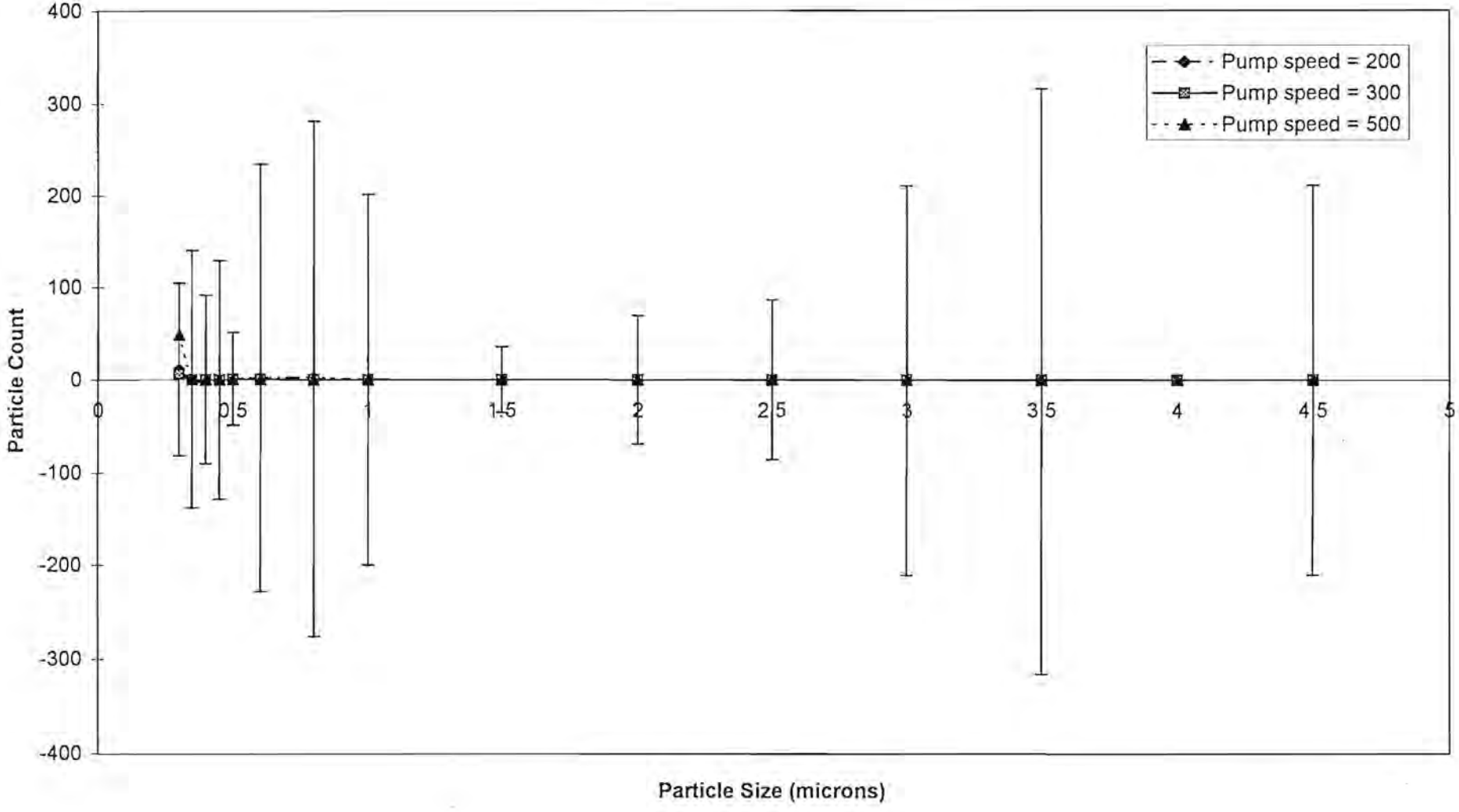
Graph 9:
MCN at Ar = 200 kPa



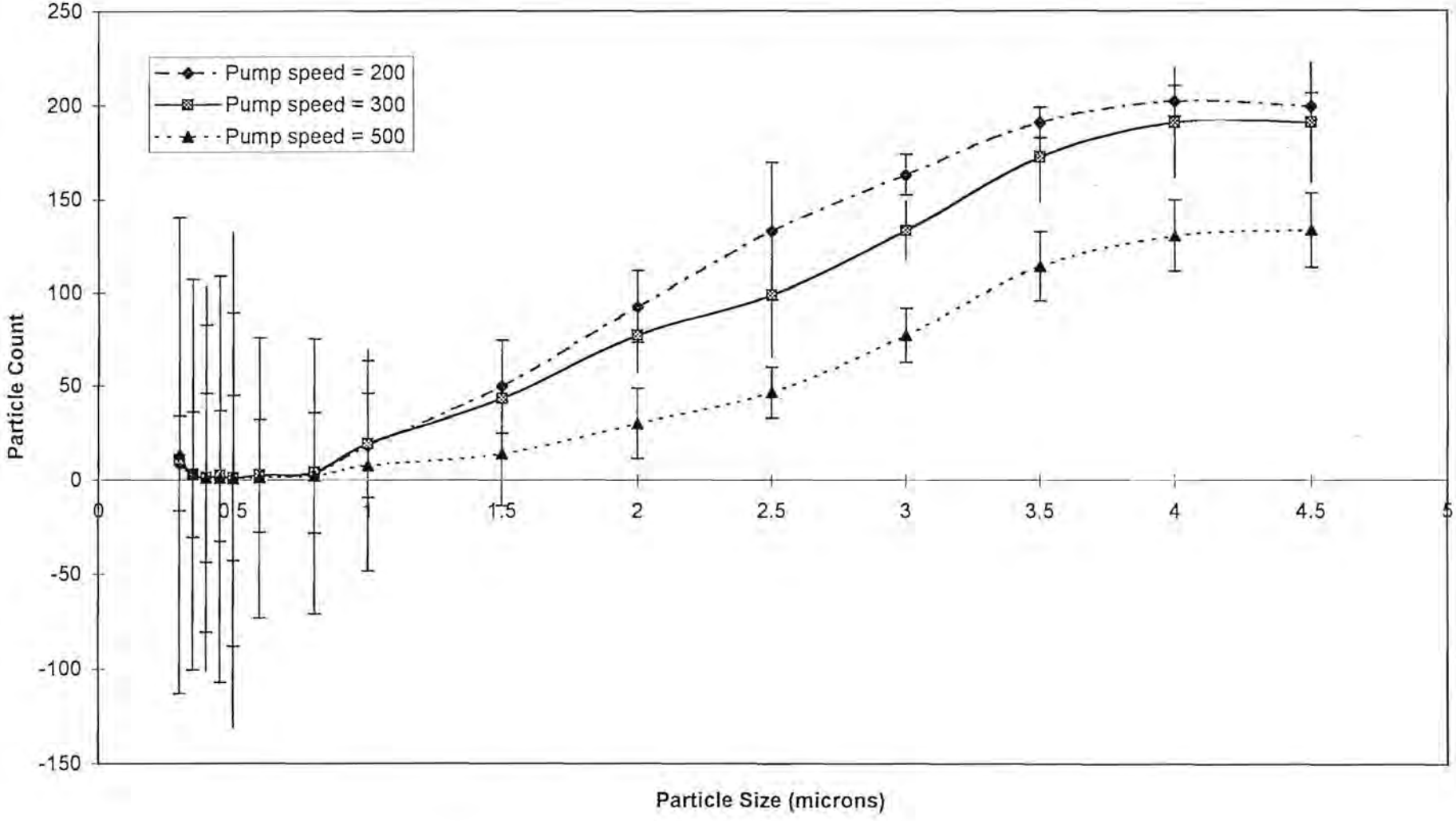
Graph 10:
Meinhardt at Ar = 200 kPa



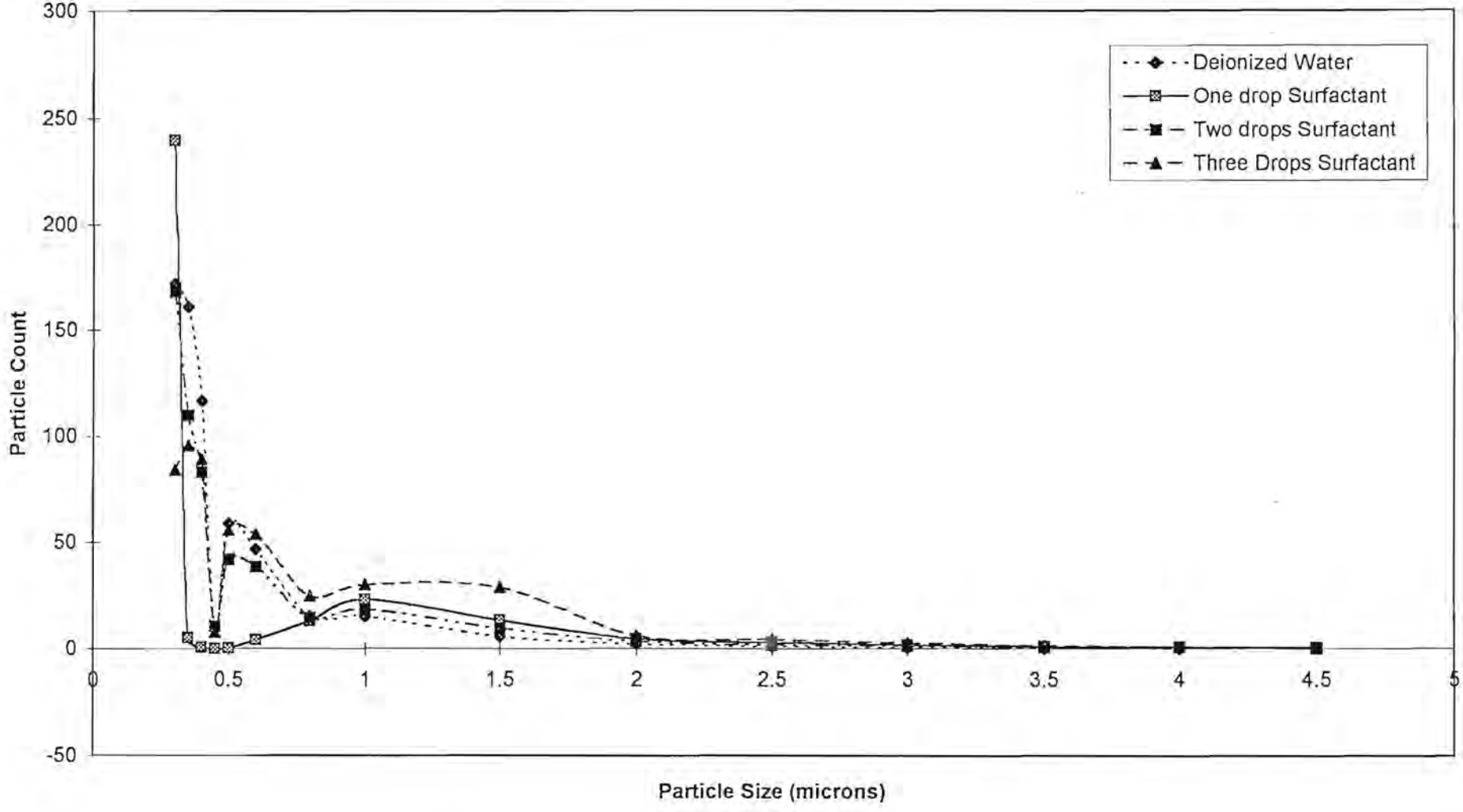
Graph 11:
V-Groove at Ar = 200 kPa



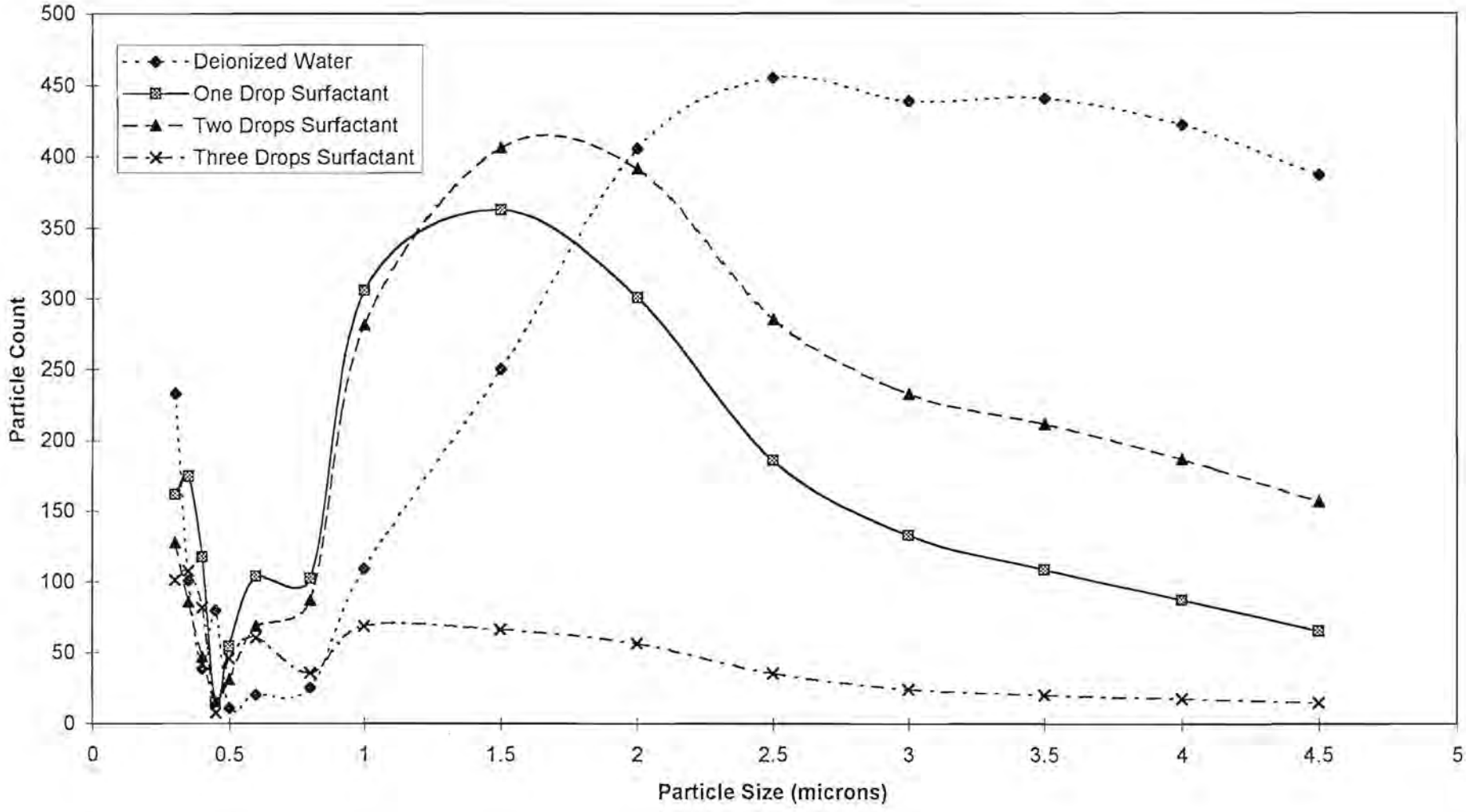
Graph 12:
Cross-Flow at Ar = 200



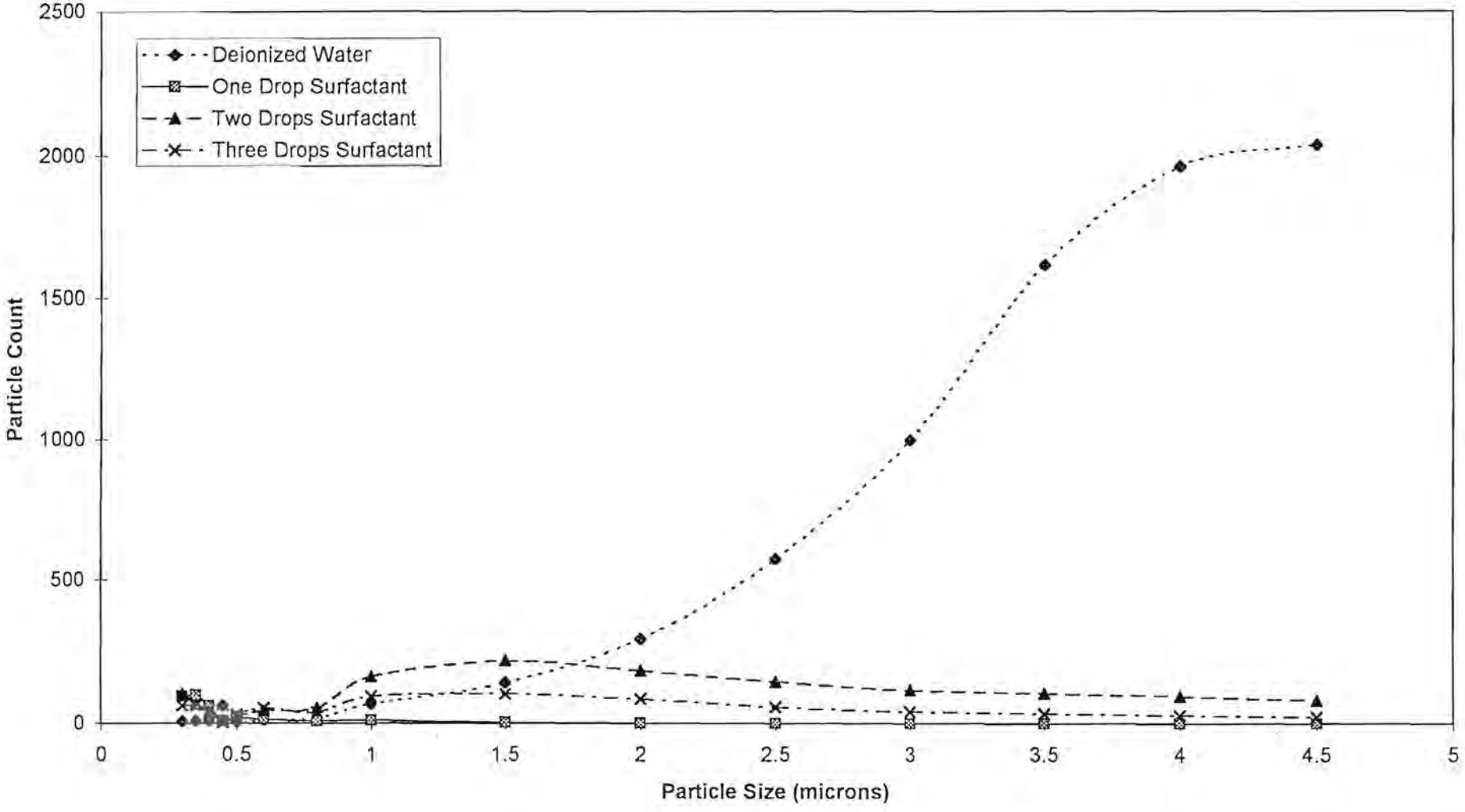
Graph 13:
Effect of Surfactant: MCN at Ar = 30 kPa



Graph 14:
Effect of Surfactant: MCN at Ar = 140 kPa



Graph 15:
Effect of Surfactant: MCN at Ar = 200 kPa



As expected, the use of a surfactant caused an increase in the smaller particles as can be seen in graphs 13-15. At the lower pressures, for the MCN, it is possible to see a third peak ending at our limit of detection, 0.3 μm while the peak above 1 μm decreases dramatically in size. At 200 kPa, however, no peak is clearly in evidence over the entire range (there is a remnant of the secondary peak). Presumably, at these levels, the solution is nebulized into particles smaller than 0.3 μm.

By varying the pressure of the argon gas while keeping the same solution flow rate, it is possible to see that the initial peak shifts to the left, ie. towards a smaller droplet diameter. The secondary peak does not seem to have any definite pattern relating it to the argon pressure for either the MCN or Meinhard nebulizers. In the case of the MCN, the optimal operating argon pressure for a pump speed of 200 rpm seems to be 100 kPa. When the data for the Meinhard is considered, this optimum shifts to a pressure of 200 kPa for a pump speed of 300 rpm.

4.4 Discussion of limits of detection:

Although an attempt was made at determining the limits of detection for the MCN, the ICP was recalled by SMM Instruments, from whom it was on loan, and this data could not be confirmed. The preliminary tests did show that the MCN had a great impact in lowering the background emission, by a factor of 5 in some cases. Unfortunately, this improvement was countered by a similar decrease in the analyte's peak height. In the case of a weakly emitting analyte such as Sulphur, this meant that there was no apparent improvement on the signal

to noise ratio while, for arsenic the improvement could be seen. The major gain from the MCN over the Meinhardt nebulizer was the level of solution required to run an analysis: 1 ml as opposed to 5 ml in our case. This means that the MCN should come into its own when only low volumes of solution are available, as is often the case in environmental samples.

4.5 References

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Chapter 5

Extraction and speciation of Arsenic

5.1 Introduction:

As mentioned previously, there are several methods for the extraction and speciation of arsenic. These would be too numerous to fully explore within this dissertation. Therefore, only one method was followed. Most arsenic studies involving soil samples follow the hydride generation method. In this case however, the method chosen was that of solvent speciation followed by sequential resin speciation, which is usually used for marine samples. The reason for this was two fold. Primarily, the availability of reagents and equipment and secondarily, the availability of expertise. Ion exchange resins were readily available within the research group as well as suitable solvents for the solvent extraction step. At the same time, a few people within the Department of Chemistry, University of Pretoria, had already dealt with ion exchange, specifically with these resins which gave us an advantage when using them. Hydride generation on the other hand had not yet been performed at this university and would have required the purchasing or manufacture of specialized glassware. Also, hydride generation is a less sensitive method and uses more reagents. A the same time, other researchers tried to analyze the level of arsenic in soils by working out the total concentration of arsenic by reducing As (V) to As (III) and subtracting from this the level of As (III) found previously. This method, however, proved to be highly inefficient and unreliable.

5.2 Experimental 1: Ion exchange

Initially, 0.922g of Dowex 1x8 anion exchanger was slurry loaded in a tube (blue/orange code). This gave us a resin length of 15cm. This resin was conditioned as described below. Various concentrations of As (V) were prepared from a 1000 mg/L stock solution. The resin was washed prior to the run with 50 ml 1 M HCl followed by 50 ml de-ionized water. The "sample" was run through and then stripped from the resin with 100 ml of 1 M HCl. The resin was then washed again in preparation for the next run.

Results and discussion:

From graph 1, it is possible to see the effect of HCl on the Arsenic loaded resin. Although it might be argued that 80 ml might have been sufficient to completely remove the arsenic from the resin, it was decided to use a larger volume, partially for ease of preparation and also to ensure that all the arsenic was removed. This is due to the fact that not all the resins which were prepared had the same mass, a result of the difficulty of reproducibly slurry-loading these resins. In effect, this larger volume yielded a greater margin of error in the weighing of subsequent resins. Should a larger amount of resin be used, there would still be enough HCl to strip it completely clean of arsenic. The resin could hold approximately 13 mg of As, as can be seen from graph 2. As the research progressed, it became apparent that a new resin would have to be used after about 50-60 runs as the percent recovery of As dropped. This could be due to the acid used destroying the resin or, from the resin binding sites becoming irreversibly bonded with As or other metals over time.

5.3 Experimental 2: solvent extraction

A stock solution of As (III) was prepared in 1 M HCl. Individual standards of As in 100 ml of 11 M HCl were prepared from this stock solution. These were then extracted with 4x 25 ml of an organic solvent. These portions were combined and extracted with 2x 50 ml of de-ionized water.

Results and discussion:

The purpose of this section was to convert the As (III) in its inorganic form to $AsCl_3$ which would favor the non-polar organic phase. As was expected the more non-polar solvents were better at extracting the $AsCl_3$. From graph 3, we can see that there is little difference between benzene and cyclohexane. However, hexane did not do as well. Toluene was also a pretty good extractor and has the advantage of being less harmful than benzene. In the end, benzene was selected as it was the purest, most readily available solvent in the stores at the time.

5.4 Experimental 3: soil samples, extraction of As(III) and As(V)

Soil samples weighing 5 g were spiked with both As (III) and As (V) and left to air-dry. These were subsequently milled and mixed with 100 ml of HCl at different concentrations. The sample was then made up to 11 M HCl and solvent extracted with 100 ml of benzene. The organic phase was then back extracted with 100 ml de-ionized water. The aqueous phase was neutralized back to a pH of 7 with NaOH and filtered with a Whatman 4 filter. It was then passed through the resin using the method discussed above.

Results and discussion:

From these tests, it soon became apparent that the ideal conditions not involving a microwave digestion step would use 11 M HCl. The soil was visually better digested and at the same time, the As (III) was converted to $AsCl_3$ without the need for additional steps prior to the solvent extraction. This meant less wet chemistry and therefore better chances at achieving accurate results. From the table below, it is possible to see that the recovery rates were very good, almost all falling within a range of 95-100%.

TABLE 1: Recovery of As (III) and As (V) from spiked soil samples.

Sample No	1	2	3	4	5
Weight of soil (g)	5	5	5	5	5
Spike As (V) (g)	10.111	10.111	10.111	10.111	10.111
Recovery (g)	9.604	9.809	9.780	9.675	9.966
% Recovered	94.99	97.01	96.73	95.69	98.57
Spike As (III) (g)	10.001	10.001	10.001	10.001	10.001
Recovery (g)	10.036	9.847	9.778	9.933	9.843
% Recovered	100.35	98.46	97.77	99.32	98.42

5.5 Experimental 4: soil samples, extraction of MMAA

Soil samples (5 g) were spiked with As (III) and As (V) as well as MMAA. These were acid digested with 11 M HCl, filtered and then extracted with 100 ml Benzene. The organic layer was back extracted with 100 ml de-ionized water while the aqueous layer was neutralized with NaOH, filtered with a Whatman 4 filter and then passed through the anion exchange resin. The resin was then first eluted with acetic acid / sodium acetate mixture (1:1, 50 ml) followed by 100 ml 1 M HCl.

Results and discussion:

MMAA is readily stripped from the Dowex resin with an acetic Acid / sodium acetate mixture while As (V) is not. Therefore, it is possible to elute them separately by choosing the acids carefully. This method in effect allows us to speciate all the various type of As commonly found in soils: As (III), As (V), MMAA and DMAA. DMAA has a more basic character and therefore will be retained only by the cation exchange resin used in series with the anion exchanger. The eluent tested at the end of this sequence showed no detectable trace of As, even after being evaporated down to 10 ml (10 % of initial volume). The recovery rates of this experiment are shown below in table 3. As DMAA could not be obtained commercially at the time, it was not possible to test the accuracy of the recovery process.

Table 2: Recovery values of As for spiked soil samples.

Sample No	1	2	3	4	5
Weight of soil (g)	5.003	5.122	5.056	5.021	5.035
Spike As (V) (g)	10.009	10.009	5.004	1.001	6.005
Recovery (g)	9.644	9.770	5.016	1.015	5.983
% Recovered	96.35	97.61	100.23	101.42	99.63
Spike As (III) (g)	9.998	9.998	4.999	0.999	5.998
Recovery (g)	9.374	9.640	4.784	0.984	5.857
% Recovered	93.76	96.42	95.69	98.50	97.65
Spike MMAA (g)	1.006	1.006	0.503	0.503	0.503
Recovery (g)	1.003	.995	0.468	0.504	0.751
% Recovered	99.70	98.90	93.04	100.20	99.47

5.6 Experimental 5: phosphoric rock and fertilizers

Phosphoric rock samples were obtained from Palaborwa, as well as Phosphoric Acid samples from Indian Oceans Fertilizers. Fertilizer samples were also obtained from commercial sources as well as from a farm. These were spiked with both As (III) and As (V) and then, were all acid digested in 11 M HCl, filtered and solvent extracted with benzene. The organic phase was then back extracted into de-ionized water while the aqueous phase was neutralized with NaOH. The neutral aqueous phase was then filtered twice, initially with a Whatman 42 filter and then with a Whatman 4 filter. The filtrate was then passed through the anion exchange resin followed by the cation exchange resin. The arsenic fractions were then released from the resin as described previously.

Results and discussion:

These samples caused quite a few problems. Primarily, phosphate rock can very efficiently be digested by HCl. Indeed, the reaction tended to be violent should too much HCl be added at once. After 2 hours, on average, most of the rock would be dissolved, leaving behind a tiny amount of very fine powder residue which could not be weighed. Unfortunately, when these solutions were neutralized, a thick white precipitate (presumably sodium hypophosphite) tended to be formed at a pH of 6.5 – 6. This was a particularly troublesome event as the finer filter paper tended to get clogged while the larger filter paper did not remove this precipitate sufficiently well. One method by which this was solved was to do a double filtration.

Early ICP-AES tests of this precipitate, run by re-dissolving the precipitate in HCl showed that up to 8 % of the As (V) could be found within it, while the precipitate appeared to be largely composed of phosphorus. This indicates a strong possibility of a phosphate based salt. As it was thought that this phenomenon was due to the close relationship between P and As, and, as phosphate tends from an insoluble precipitate with OH^-, the neutralizing base was then changed to ammonia. This caused a lower level of precipitation, as well as, only 3-5 % of the Arsenic (V) being co-precipitated (table 3).

Using Celite as an alternative filter proved to be more effective, allowing for a "hot" filtration, as vacuum filtration is much faster than gravitational filtration.. When the Celite bed was dissolved, the level of As (V) found dropped to 1-3.5 %. However, the Celite could only be used once due to contamination from the co-precipitated As (V). For this reason, as well as the cheaper cost and greater availability of filter paper, this filtration method was abandoned.

Table 3: Results from the digestion of Phosphoric rock.

Sample No:	Weight: (g)	spike mg/kg As (III) As (V)	recovery mg/kg As (III) As (V)	% Recovery As (III) As (V)	Filtration method % As in residue	Base used
1	5.023	10.009 10.023	9.951 9.543	99.42 95.21	Filter paper 4.56	NaOH
2	5.001	10.009 10.023	9.837 9.653	98.28 96.31	Filter paper 4.01	NaOH
3	5.012	10.009 10.023	9.976 9.756	99.67 97.34	Filter paper 3.02	NaOH
4	4.999	10.009 10.023	9.776 9.231	97.67 92.11	Filter paper 7.68	NaOH
5	5.008	10.009 10.023	9.863 9.495	98.54 94.73	Filter paper 5.02	NaOH
6	5.004	9.899 10.023	10.043 9.879	101.45 98.56	Celite 1.00	NH_4^+
7	5.015	9.899 10.023	9.843 9.609	99.43 95.87	Celite 3.42	NH_4^+
8	5.045	9.899 10.023	9.558 9.767	96.56 97.45	Celite 2.97	NH_4^+
9	4.970	9.899 10.023	9.735 9.746	98.34 97.24	Celite 2.31	NH_4^+
10	5.002	9.993 10.012	9.966 9.556	99.73 95.45	Celite 3.34	NH_4^+
11	4.998	9.993 10.012	9.249 9.657	92.56 96.45	Filter paper 4.23	NH_4^+
12	4.978	9.993 10.012	9.721 9.787	97.28 97.75	Filter paper 2.96	NH_4^+
13	5.053	9.993 10.012	9.922 9.549	99.29 95.38	Filter paper 4.39	NH_4^+
14	5.021	9.993 10.012	10.146 9.614	101.53 96.02	Filter paper 3.64	NH_4^+
15	5.006	9.993 10.012	9.885 9.638	98.92 96.26	Filter paper 3.26	NH_4^+

Table 4: Results from fertiliser spikes.

Sample No	Weight: (g)	spike mg/kg As (III) As (V)	recovery, mg/kg As (III) As (V)	% Recovery As (III) As (V)
1	5.006	9.997 10.003	9.732 9.568	97.35 95.65
2	5.009	9.997 10.003	9.795 9.727	97.98 97.24
3	5.011	9.997 10.003	9.926 9.759	99.29 97.56
4	4.899	9.997 10.003	9.972 9.856	99.75 98.53
5	5.00	9.997 10.003	9.854 9.796	98.57 97.93

From Hydride Generation experiments conducted by the mining companies which provided us with some phosphate rock samples, the levels of As (III) (as As_2O_3) for two types of rocks, A and B, are known to be 13 mg/Kg and 15 mg/Kg respectively. There was a good correlation between these two techniques as the values obtained for these two rocks in this experiment were 12.4 mg/Kg for rock A and 15.6 mg/Kg for rock B. Unfortunately, the levels of As (V) were not determined by Hydride Generation and therefore cannot be compared.

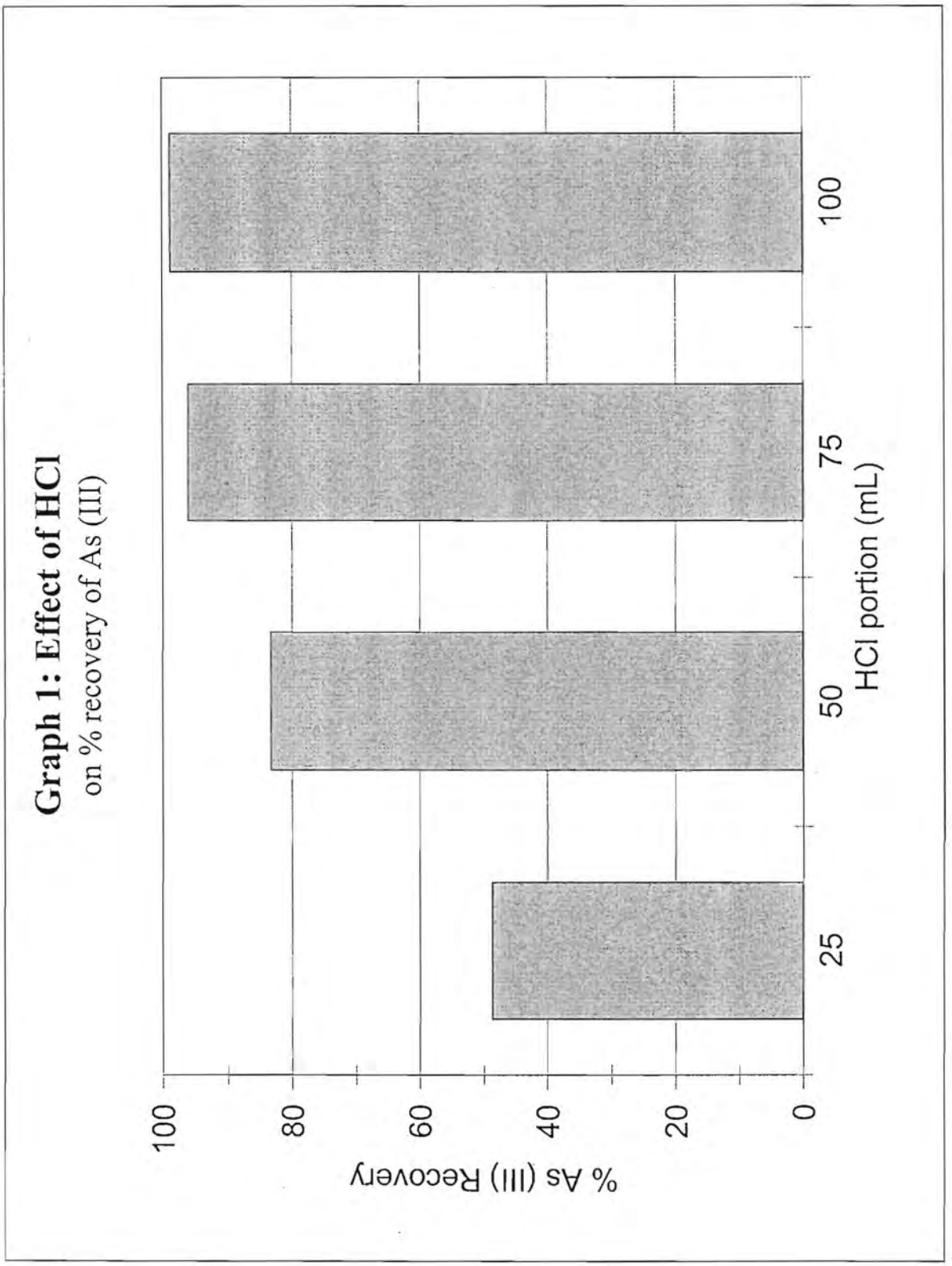
5.7 Experimental 6: new method for analysing phosphorus bearing rocks

Phosphorus bearing rock samples were spiked with As (III), As (V) and MMAA, then they were digested in 11 M HCl. These solutions were solvent extracted with benzene as described above and then the aqueous phases were neutralized. The neutral solutions were then re-acidified to 1 M acetic acid, using a sodium acetate buffer. The solutions were then passed through the resin, and the arsenic was then released from the resin as described above.

Results and discussion:

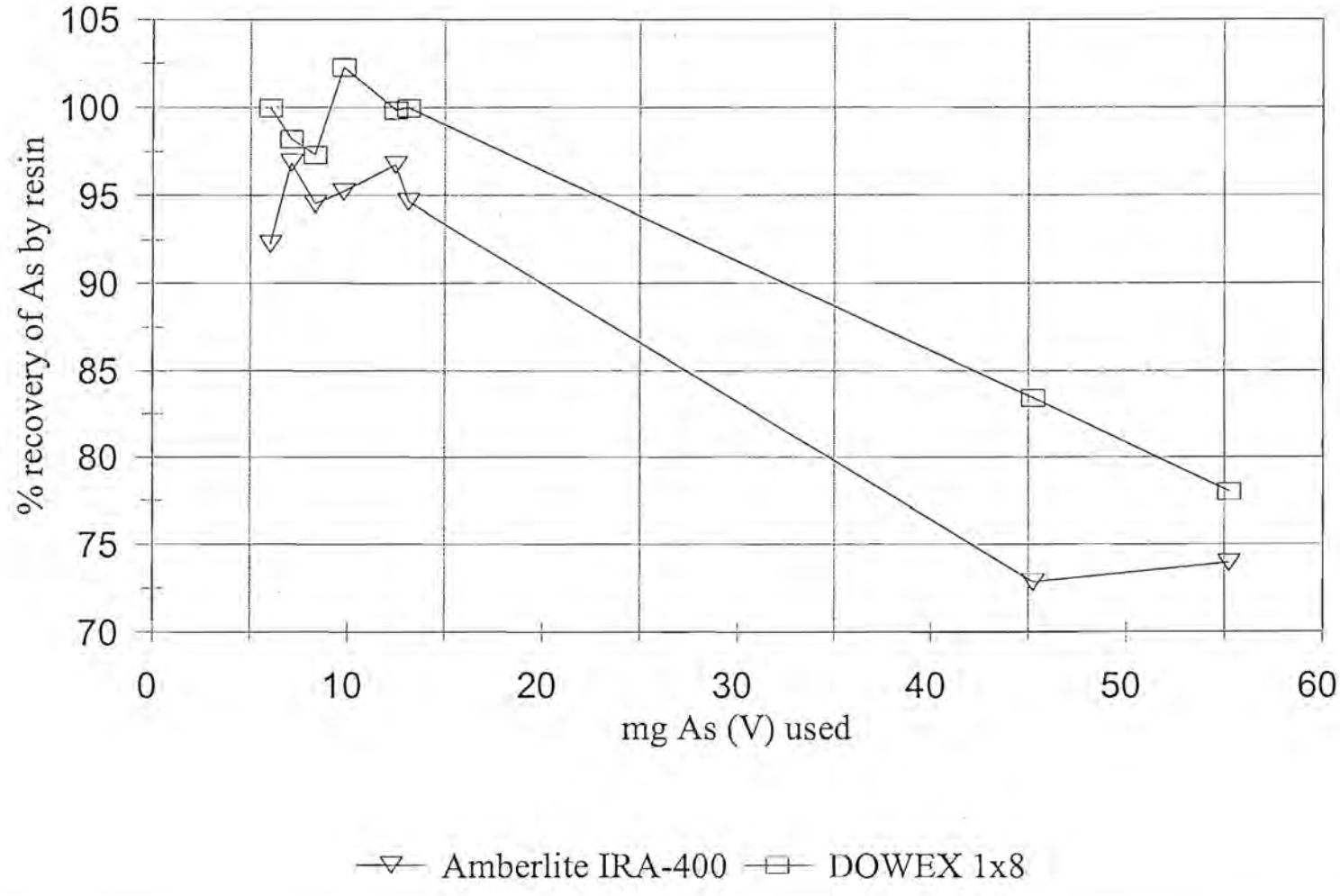
Due to the difficulties in dealing with the white precipitate, a new method had to be developed. The easiest was to reverse the order of resin speciation. In theory, only the DMAA should be the only form of As to be retained by the cation exchange resin while the As (V) and MMAA will be retained by the anion exchange resin. Therefore, if the solution were to be prepared with acetic acid, under the right conditions, the resin should not retain the MMAA. As the As (V) is more tightly bound to the resin and will be only displaced by the HCl, it stood to reason that with this method, the As (III) would be found in the benzene, the As (V) would remain in the resin while the MMAA would be in the eluent. This could have been further tested by passing the solution through a cation exchange resin which would retain the DMAA, leaving the MMAA in the solution. This method raised the overall recovery of As by 3% on average which may not seem great though it did simplify the overall process by removing the hot filtration stage when using Celite and the double filtration stage when using filter paper.

Graph 1: Effect of HCl
on % recovery of As (III)

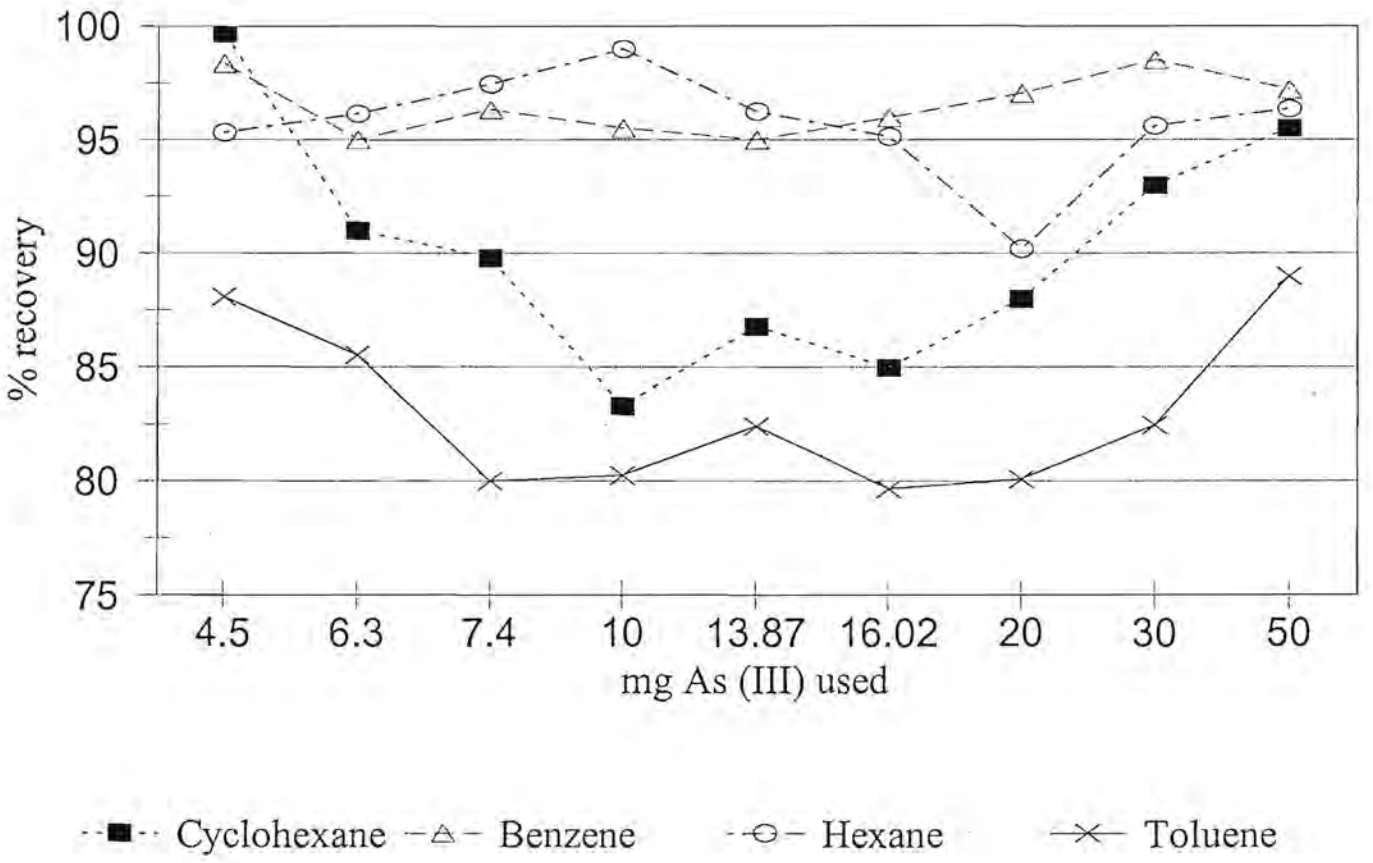


Graph 2: Comparison of As recovery

by two anion exchange resins



Graph 3: Comparison of % recovery
of As by different organic phases



Chapter 6

General Conclusions

The driving force of this study was the need for a study of viable methods of analysing arsenic in soils, fertilisers and phosphorus bearing rocks through the use of Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES). This technique has come into its own in recent years due to its speed, sensitivity and multi-element capabilities, as an analytical method for the determination of many elements in a wide variety of matrices. Its benefits have rendered it the mainstay of many analytical laboratories in the environmental, health and general industrial areas.

As a counterpoint, most analytical techniques, especially spectroscopy related methods, still can have difficulties with the accuracy of the measurements. These techniques need to be both accurate and precise. While several procedures such as standard addition have been developed to overcome the matrix effects, the application of spectroscopic techniques can still be complicated and there is certainly room for improvement both in accuracy and standardization. To this end new methods of sample introduction are constantly developed.

In chapter 4, we looked at one of these improvements, the Micro-Concentric Nebulizer. While this nebulizer does provide some definite advantages in decreasing the plasma loading and generating a finer aerosol, some inherent drawbacks are inevitable. The gain in lowering

background radiation is somewhat offset by the loss in signal intensity. There is however a benefit to this nebulizer. Its smaller capillaries allow for smaller solution volumes required in a typical analysis, thus making it ideal for studies involving low sample quantities. The nebulizer's ideal operating conditions were explored, showing that the aerosol's physical properties were indeed dependent on the gas flow rates and sample flow rates.

The internal dimensions of the Micro-Concentric Nebulizer required some special glassware to be designed to prevent blockages due to suspended particles in the solutions. This glassware was developed with ease of use and possible solution quantities in mind. Indeed the glassware was optimized for low quantities, ranging for 0.5 ml to 8 ml.

The sheer dynamic range (up to 5 or 6 orders of magnitude) and high precision as well as powerful software and reproducible wavelength changes have made the ICP-OES the favoured technique for multi-element analysis. The technique also lends itself well to automation, making the analysis of large numbers of sample relatively easy. Thus the technique has gained popularity in areas such as environmental, hospital and process laboratories.

This ease of automation and popularity for environmental analyses prompted the second part of the study, the analysis of arsenic in soils, rocks and fertilisers. Although the ICP-OES was mainly used as a detector, with most of the wet chemistry having already been done, a similar study requiring only the overall levels of arsenic would be simple to implement. The major

advantage of the ICP-OES in this study was the relative freedom it allowed from matrix effects. This meant that the different extraction methods could more easily be compared. Both the lines used were free from interference, though this was mainly due to the sample preparation stages.

Ion exchange chromatography was shown to be an effective way of speciating the major forms of arsenic in combination with solvent extraction. By reversing the order of ion exchange, the method could be simplified with a slight gain in recovery levels. Different filtration methods were shown to be effective. At the same time, the effect of the bases used to neutralize the solutions was explored. These played a role in the precipitation of phosphorus which hampered the analysis in some cases. By the simple act of changing the base to one in which phosphate salts were more soluble, the level of precipitation dropped visibly. At the same time, the level of Arsenic being co-precipitated dropped as seen in chapter 5, table 3.

Different organic phases were shown to have different extraction capabilities towards As(III) in the form of $AsCl_3$ which was to be expected based on their polarity. On average, the more polar the organic phase, the less well it extracted the $AsCl_3$.

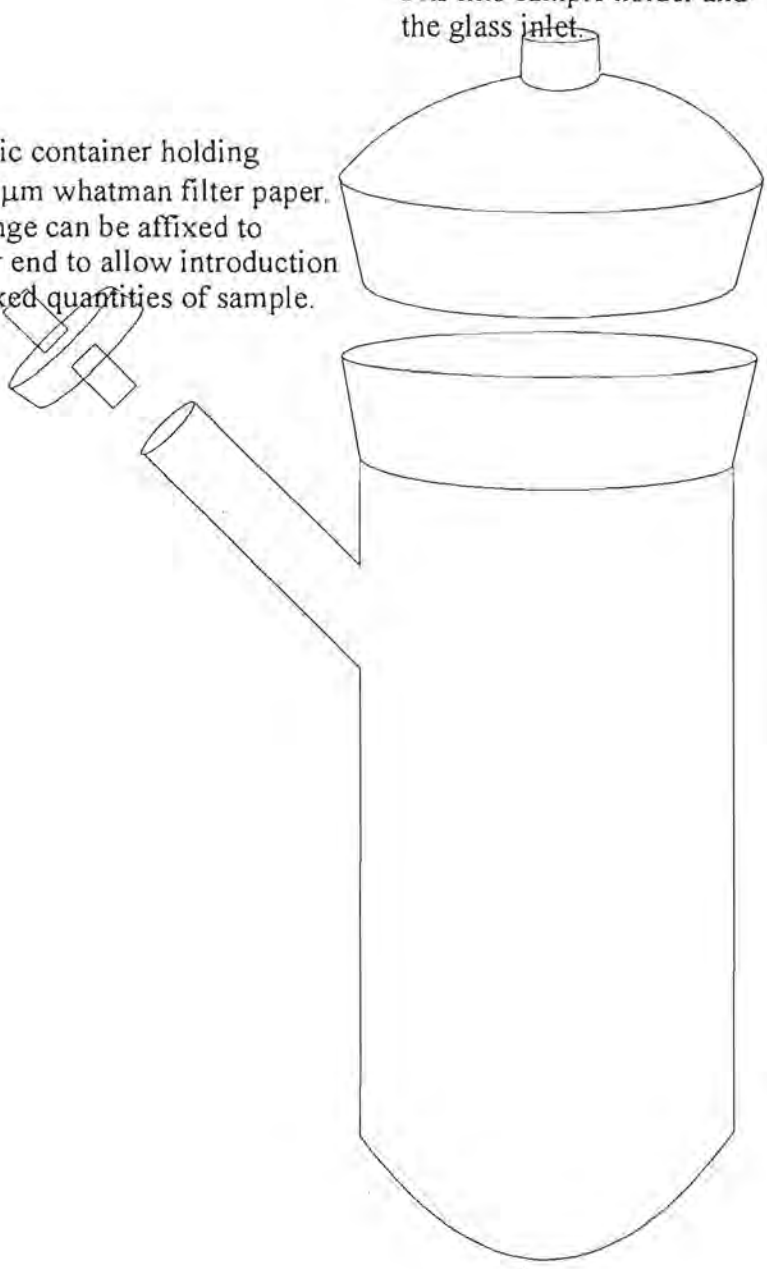
After optimization of the system, standard addition experiments were done, yielding excellent recovery rates. From the experiments carried out, a reasonable level of precision and accuracy was possible with this system as can be seen from chapter 5, table 4. However, the sample

preparation steps tended to be tedious and often took up to five hours due to the filtration steps and pumping solvents through the ion exchange tubing. However in cases where more than one sample needs to be run, several samples could be run through the ion exchange step simultaneously, by using more advanced pumps, thus reducing the overall sample preparation time.

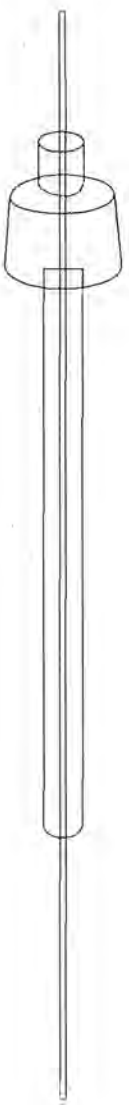
In conclusion, it is clear that ICP-OES is a strong contender in the determination of arsenic in the environment though some more work should be done in the speciation and extraction of arsenic. Currently, hydride generation, with all its drawbacks may still be the most efficient method to use. Unfortunately, the ICP was lost before such premises could be fully explored.

Glass double ended lid.
Fits into sample holder and
the glass inlet.

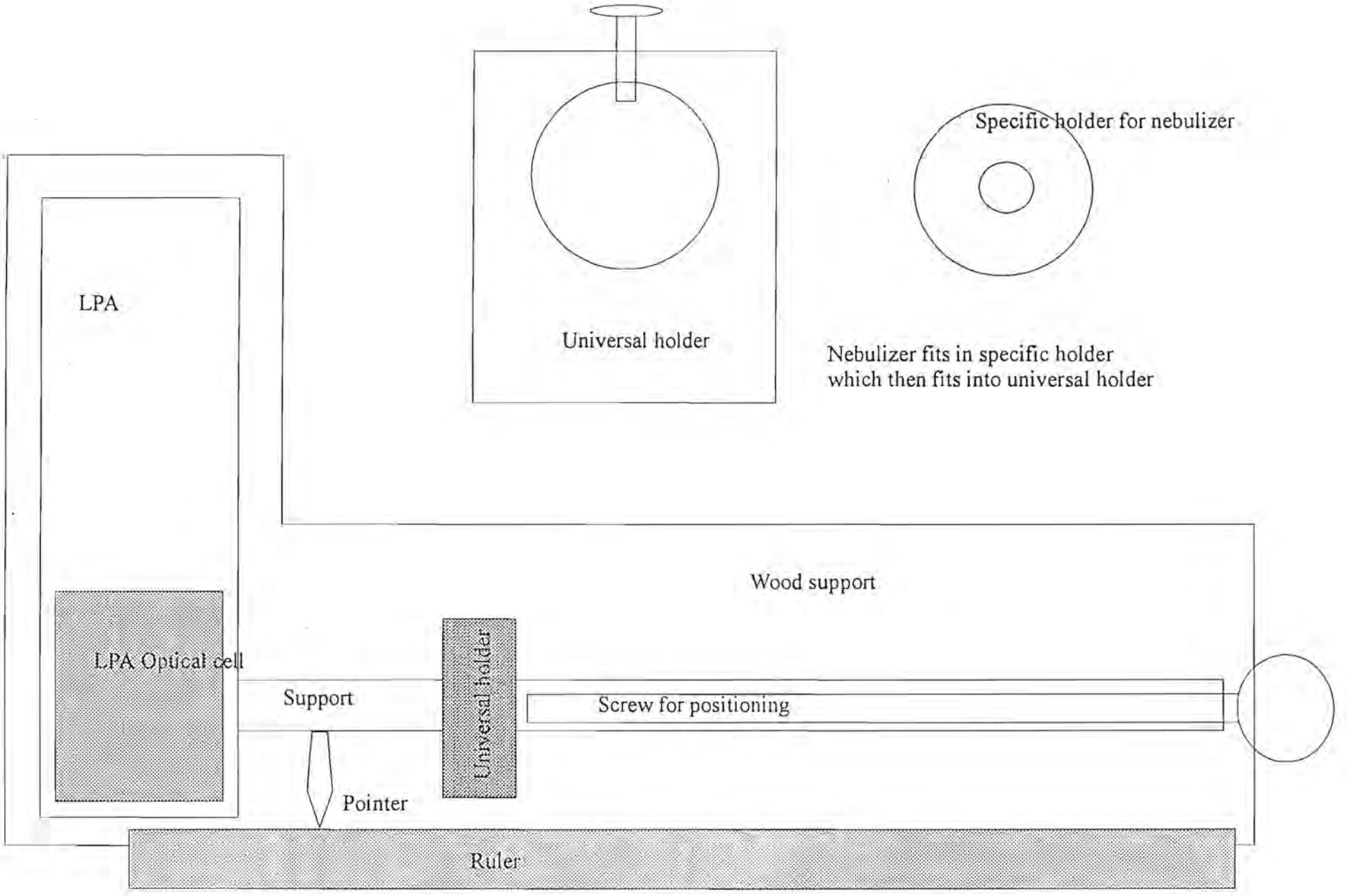
Plastic container holding
0.45 µm whatman filter paper.
Syringe can be affixed to
other end to allow introduction
of fixed quantities of sample.



Sample holder



Glass inlet which fits into sample holder. Thin tube fits into the glass inlet, thus enabling the sampling of many solutions by moving the glass inlet from sample holder to sample holder. A glass cap has been designed along similar lines for the sample holders not currently used.



By turning the screw for positioning, the nebulizer
can be placed at a specific distance from the optical cell.