Advance Analytical Course

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Lecture No. # 23

If we compare the different methods of analysis of metal and metalloid, and we start comparing the different machines that I used – the ICP-MS, the ICP-AES and the AAS, you will see from this graph that it is that ICP-MS is the best method and has the most efficient analysis after even enrichment.

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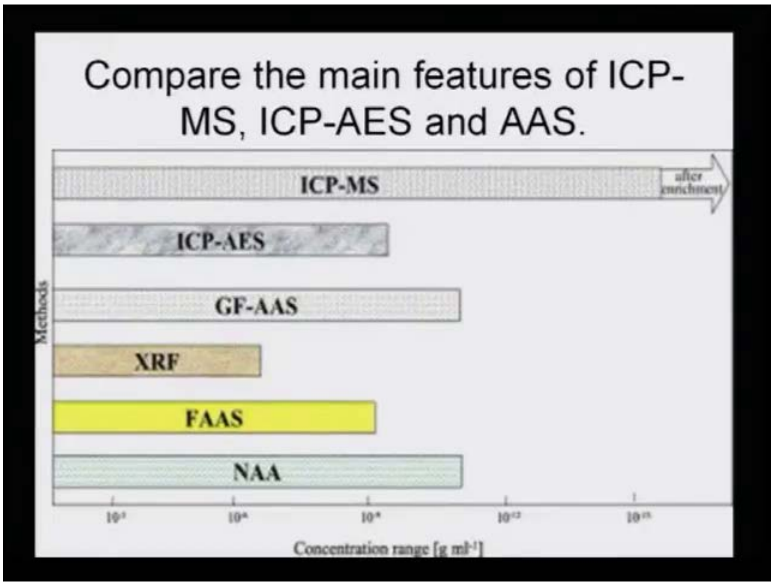

Compare the main features of ICP-MS, ICP-AES and AAS.

Then, comes the ICP-AES, which is slightly inferior to graphite furnace ASS. And the last one is the flame ASS. So, one can see that if one sits to compare the efficiencies, the sensitivities, and the enrichment of the trace and trace metal, ultra-trace metal analysis, one finds that ICP-MS is the answer.

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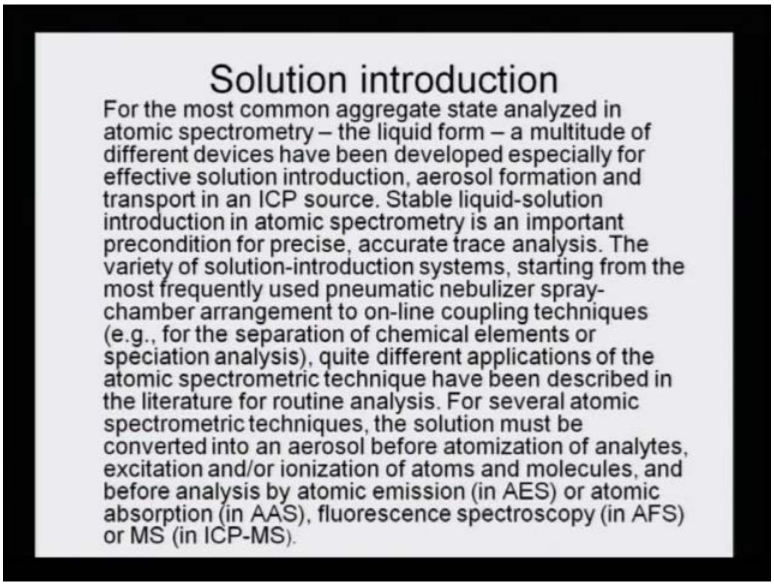

Solution introduction

For the most common aggregate state analyzed in atomic spectrometry – the liquid form – a multitude of different devices have been developed especially for effective solution introduction, aerosol formation and transport in an ICP source. Stable liquid-solution introduction in atomic spectrometry is an important precondition for precise, accurate trace analysis. The variety of solution-introduction systems, starting from the most frequently used pneumatic nebulizer spray-chamber arrangement to on-line coupling techniques (e.g., for the separation of chemical elements or speciation analysis), quite different applications of the atomic spectrometric technique have been described in the literature for routine analysis. For several atomic spectrometric techniques, the solution must be converted into an aerosol before atomization of analytes, excitation and/or ionization of atoms and molecules, and before analysis by atomic emission (in AES) or atomic absorption (in AAS), fluorescence spectroscopy (in AFS) or MS (in ICP-MS).

Now, in all of these, the solution introduction is the most crucial step for most common aggregate state analyzed in atomic spectrometry – the liquid form – a multitude of different devices have been developed especially for effective solution introduction, aerosol formation and transport in an ICP source. So, there are three different issues that need to be addressed or to be understood how the solution is being introduced. That means whether a peristaltic pump is being used or a pneumatic pump is being used, and so on and so forth. Then, how is the aerosol being formed or the mix of the standard solution being formed or the sample solution being formed? And, how is it getting transported in that ICP source?

Stable liquid solution introduction in atomic spectrometry is an important precondition for precise, accurate trace analysis. The variety of solution introduction system starting from the most frequently used pneumatic nebulizer spray-chamber arrangement to on-line coupling techniques, that is, for the separation of chemical elements or speciation analysis, quite different applications of the atomic spectrometric techniques have been described in the literature for routine analysis. For several atomic spectrometric techniques, the solution must be converted into an aerosol before atomization of the analytes, excitation and/or ionization of atoms and molecules, and before analysis by atomic emission, that is, in AES or atomic absorption (in AAS), fluorescence spectrometry (in AFS) or MS, that is, the mass spectrometry. So, three things must take place while analyzing on these ICPs or AAS machine. And, that is, the atomization of the analyte, its excitation and ionization, and finally, its identification by means of either atomic emission or atomic absorption or fluorescence or mass spectrometry.

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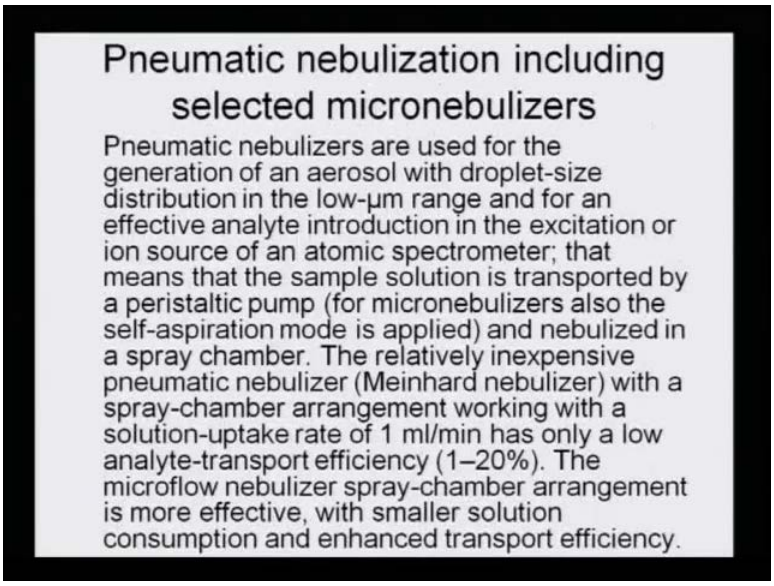

Pneumatic nebulization including selected micronebulizers

Pneumatic nebulizers are used for the generation of an aerosol with droplet-size distribution in the low-µm range and for an effective analyte introduction in the excitation or ion source of an atomic spectrometer; that means that the sample solution is transported by a peristaltic pump (for micronebulizers also the self-aspiration mode is applied) and nebulized in a spray chamber. The relatively inexpensive pneumatic nebulizer (Meinhard nebulizer) with a spray-chamber arrangement working with a solution-uptake rate of 1 ml/min has only a low analyte-transport efficiency (1–20%). The microflow nebulizer spray-chamber arrangement is more effective, with smaller solution consumption and enhanced transport efficiency.

Now, pneumatic nebulization including selected micronebulizers – now, these again… Time and again, I have told that different methodologies are adapted for best kind of analytical method development. And, for that, if special considerations of the machines have to be taken, then they are definitely designed accordingly. Pneumatic nebulizers are used for the generation of an aerosol with droplet-size distribution in the low micrometer range and for an effective analyte introduction in the excitation or ion source of an atomic spectrometer. So, why was there a need for a pneumatic nebulizer? The need for pneumatic nebulizer came into being, because very small sized droplets and the aerosol had to be prepared in order for the sample introduction, and as low as micrometer range had to be effectively produced. And, for that, pneumatic nebulizer was the only answer. That means that the sample solution is transported by a peristaltic pump for micro nebulizer also.

The self-aspiration mode is applied. So, it kind of sucks on its own. There is a self-aspiration and there is this peristaltic pump, which pushes the solution more towards the nebulizer. The nebulized and then it is nebulized in the spray chamber. So, it does not get waste. There is a proper glass spray chamber with in which the aerosol forms. The relatively inexpensive pneumatic nebulizer or the Meinhard nebulizer – the name of the nebulizer is so – with a spray-chamber arrangement working with a solution-uptake rate of 1 ml per minute has only a low analyte-transport efficiency. So, it does slowly pass the analyte, but it is very efficient and only 1 to 20 percent of the transport of the analyte takes place. The microflow nebulizer spray-chamber arrangement is more effective, with smaller solution consumption and enhanced transport efficiency. So, what is the advantage? The advantage is that these are microflow nebulizer; not too much of solution is coming. As a result, there is an efficiency of forming the aerosol in a smaller droplet size and the droplets are sufficiently large in number to be analyzed properly.

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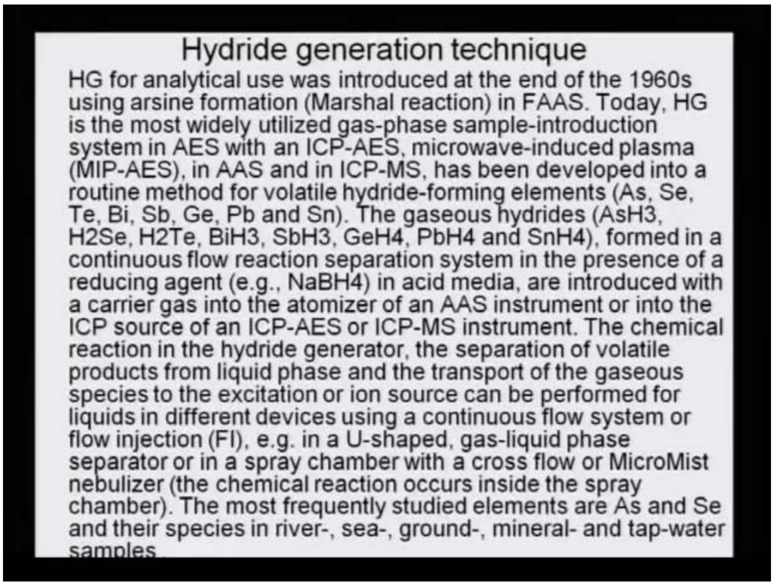

Hydride generation technique

HG for analytical use was introduced at the end of the 1960s using arsine formation (Marshal reaction) in FAAS. Today, HG is the most widely utilized gas-phase sample-introduction system in AES with an ICP-AES, microwave-induced plasma (MIP-AES), in AAS and in ICP-MS, has been developed into a routine method for volatile hydride-forming elements (As, Se, Te, Bi, Sb, Ge, Pb and Sn). The gaseous hydrides (AsH3, H2Se, H2Te, BiH3, SbH3, GeH4, PbH4 and SnH4), formed in a continuous flow reaction separation system in the presence of a reducing agent (e.g., NaBH4) in acid media, are introduced with a carrier gas into the atomizer of an AAS instrument or into the ICP source of an ICP-AES or ICP-MS instrument. The chemical reaction in the hydride generator, the separation of volatile products from liquid phase and the transport of the gaseous species to the excitation or ion source can be performed for liquids in different devices using a continuous flow system or flow injection (FI), e.g. in a U-shaped, gas-liquid phase separator or in a spray chamber with a cross flow or MicroMist nebulizer (the chemical reaction occurs inside the spray chamber). The most frequently studied elements are As and Se and their species in river-, sea-, ground-, mineral- and tap-water samples

We had talked about hydride generation fleetingly. Here is a little detailed account of hydride generation. Now, hydride generation is applicable both in atomic absorption as well as in ICPs. Hydride generation for analytical use was introduced in the end of the year 1960s using arsine formation, that is, the martial reaction in flame atomic absorption spectroscopy. Today, hydride generation is the most widely utilized gas-phase sample-introduction system in AES with an ICP-AES, microwave-introduced plasma, that is, MIP-AES, in AAS and in ICP-MS. So, it is popular now in all types of these metal-metalloid analytical method that is ranging from AAS to AES to ICPs and ICP-MS. And, these have been developed into a routine method for all volatile hydride forming elements. So, this is only applicable to elements, which have a tendency to form hydrides. It is not a common method that is used for all the 70 elements. So, particularly, arsenic, selenium, tellurium, bismuth, antimony, germanium, lead and tin – they have this tendency of forming gaseous hydride. And so, these are the elements, which need hydride generation as a technique for the sample introduction.

The gaseous hydride that is the AsH3, the H2Se, the H2Te, BiH3, SbH3, GeH4, PbH4 and SnH4, formed in a continuous flow reaction separation system in the presence of a reducing agent, that is, sodium borohydride in acidic media, are introduced with the carrier gas into the atomizer of an ASS instrument or into the ICP source of an ICP-AES or ICP-MS instrument. So, what it does? It simultaneously converse the ionic metal into its hydride and the reducing agent used here is sodium borohydride. And, there is a carrier gas, which makes it flow into either the flame of the AAS or the graphite furnace of the ASS or into the ICP source of the ICP-AES or ICP-MS instruments.

The chemical reaction in the hydride generator, the separation of the volatile product from the liquid phase and the transport of the gaseous species to the excitation or ion source can be performed for liquids in different devices using a continuous flow system or flow injection in a U-tube, gas-liquid phase separator or in a spray chamber with a crossflow of micromist nebulizer. The chemical reaction occurs inside the spray chamber. The most frequently studied elements are arsenic and selenium and the species in river-, sea-, ground-, mineral- and tap-water samples are very readily analyzed. So, this whole process is very simplified and different types of continuous flow systems like the flow injection system, which is nothing but U-shaped glass vessel or a gas-liquid phase separator or a spray chamber, where the micromist actually reacts with the reductant to form the chemical reaction, and the volatile hydrides are then analyzed. So, this makes the whole process a very simplified process in terms of getting only one species of these transition metals, namely, the arsenic, selenium, tellurium, bismuth, antimony, germanium, lead and tin. So, you see these have a tendency to have two different types of oxidation state. And, because two different species cannot be analyzed accurately, it is the higher oxidation state species, is reduced by sodium borohydride into the lower state. So, all the total metal content then comes to one oxidation – lower state oxidation and its hydride in the form of its hydride and that is what is analyzed.

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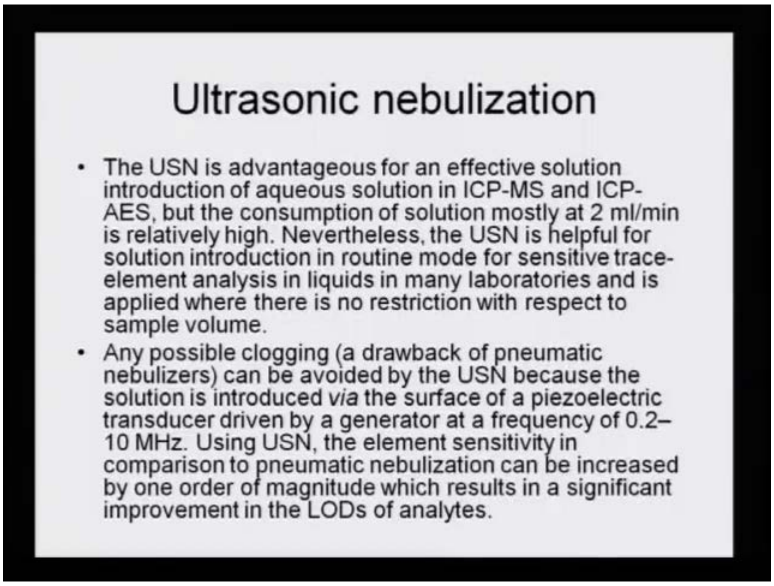

Ultrasonic nebulization

- The USN is advantageous for an effective solution introduction of aqueous solution in ICP-MS and ICP-AES, but the consumption of solution mostly at 2 ml/min is relatively high. Nevertheless, the USN is helpful for solution introduction in routine mode for sensitive trace-element analysis in liquids in many laboratories and is applied where there is no restriction with respect to sample volume.
- Any possible clogging (a drawback of pneumatic nebulizers) can be avoided by the USN because the solution is introduced *via* the surface of a piezoelectric transducer driven by a generator at a frequency of 0.2–10 MHz. Using USN, the element sensitivity in comparison to pneumatic nebulization can be increased by one order of magnitude which results in a significant improvement in the LODs of analytes.

Ultrasonic nebulizer or nebulization – the ultrasonic nebulization is also one of the nebulizing techniques and is advantageous for an effective solution introduction of aqueous solution in ICP-MS and IES. So, this is a very well-designed method only for the ICPs, but the consumption of solution mostly at 2 ml per minute is relatively high. It is very fast consuming apparatus. Nevertheless, the ultrasonic nebulization is helpful for sample introduction in routine mode for sensitive trace-element analysis in liquids in many laboratories and is applied where there is no restriction with respect to sample volume. So, this is a sensitive method and it is mainly used for trace element analysis in liquids, and especially, where there is no restriction for any kind of sample volume.

Any possible clogging, a drawback of pneumatic nebulizer can be avoided in ultrasonic nebulization, because the solution is introduced via the surface of a piezoelectric transducer driven by a generator at a frequency of 0.2 to 10 megahertz. Using ultrasonic nebulization, the element sensitivity is comparative to pneumatic nebulization, and can be increased by one order of magnitude, which results in a significant improvement in the limits of detection of the analytes. So, it has an edge over pneumatic nebulizers, and therefore, since it uses a very specialized kind of piezoelectric transducer and works at a frequency between 0.2 to 10 megahertz, it is very efficiently designed in order to improve the limits of detection in an analyte. So, it is having a kind of an edge over the pneumatic nebulizers.

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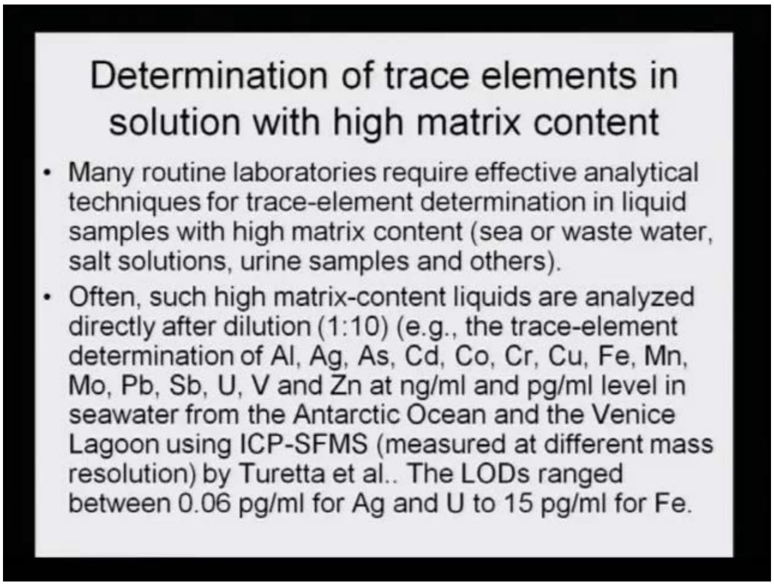

Determination of trace elements in solution with high matrix content

- Many routine laboratories require effective analytical techniques for trace-element determination in liquid samples with high matrix content (sea or waste water, salt solutions, urine samples and others).
- Often, such high matrix-content liquids are analyzed directly after dilution (1:10) (e.g., the trace-element determination of Al, Ag, As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Pb, Sb, U, V and Zn at ng/ml and pg/ml level in seawater from the Antarctic Ocean and the Venice Lagoon using ICP-SFMS (measured at different mass resolution) by Turetta et al.. The LODs ranged between 0.06 pg/ml for Ag and U to 15 pg/ml for Fe.

Determination of trace elements in solution with high matrix content – many routine laboratories require effective analytical techniques for trans-element determination in liquid samples with high matrix content, that is, sea or waste water, salt solutions, urine samples and others. Now, you will also appreciate that sea water, waste water, salt solution and urine samples have very complex matrix. And, from that complex matrix, to be able to analyze these samples and the metal-metalloid elements, it is a big challenge, because the matrix has always offered its hindrances and it has been a challenging job for the analyzer.

Often, such high matrix-content liquids are analyzed directly after dilution. So, they are diluted with 1 is to 10, and that is the trace element determination of aluminum, silver, arsenic, cadmium, cobalt, chromium, copper, iron, manganese, molybdenum, tin, lead, antimony, uranium, vanadium and zinc at nanogram per ml and picogram per ml levels in seawater from the Antarctic Ocean and the Venice Lagoon using ICP-SFMS, measured at different mass resolution by Turetta et al. has been reported. So, you see many elements at the same time have been analyzed simultaneously from a very complex seawater sample with great efficiency. The limits of detection ranged between 0.06 picogram per ml for silver, and for uranium, it was 15 picogram for iron. So, you see for uranium and silver, it was 0.06 and 15 picogram levels of iron also, could be detected from the same sample of the seawater of Antarctic Ocean. These have a certain improvement, and that is why, from time to time, furthermore improvements are brought in for making the trace element detection in very complex matrix is efficiently carried out.

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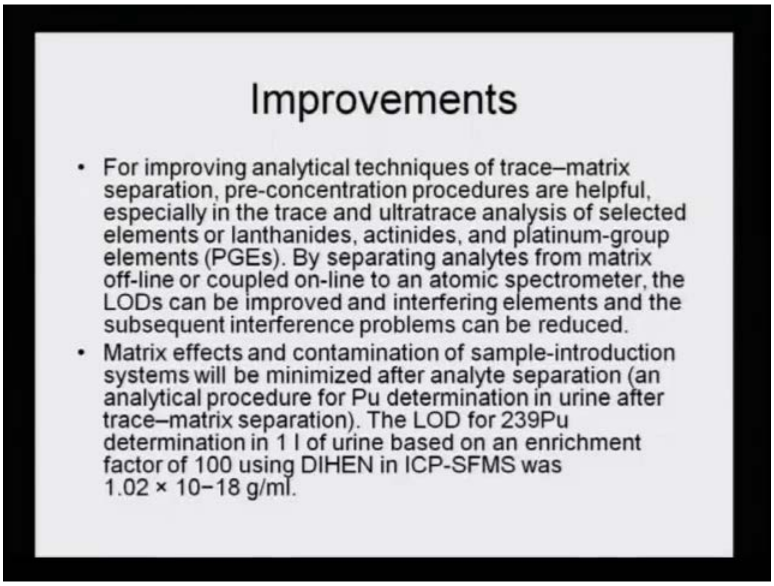

Improvements

- For improving analytical techniques of trace–matrix separation, pre-concentration procedures are helpful, especially in the trace and ultratrace analysis of selected elements or lanthanides, actinides, and platinum-group elements (PGEs). By separating analytes from matrix off-line or coupled on-line to an atomic spectrometer, the LODs can be improved and interfering elements and the subsequent interference problems can be reduced.
- Matrix effects and contamination of sample-introduction systems will be minimized after analyte separation (an analytical procedure for Pu determination in urine after trace–matrix separation). The LOD for 239Pu determination in 1 l of urine based on an enrichment factor of 100 using DIHEN in ICP-SFMS was 1.02 × 10–18 g/ml.

For improving analytical techniques of trace-matrix separation, pre-concentration procedures are helpful, especially in the trace and ultratrace analysis of selected elements of lanthanides, actinides, and platinum-group of elements, that is, the PGEs. By separating analytes from matrix off-line or coupled on-line to an atomic spectrometer, the limits of detection can be improved and interfering elements and the subsequent interference problems can be reduced. So, what does it mean? It means that for even rarer element analysis like the lanthanides, the actinides and the platinum group of elements, which are very difficult to analyze or which exists in very trace quantities, ultratrace quantities, even there, these spectrometers can be easily used the limits of detection. That means it can go down to very low levels of the presence of these elements. And, it has been found that the interfering elements also can be avoided and reduced subsequently creating a system, which is interference and problem free.

Matrix effects and contamination of sample-introduction systems will be minimized after analyte separation – an analytical procedure for Pu determination in urine after trace-matrix separation. The limit of detection for 239Pu determination in 1 litre of urine based on an enrichment factor of 100 using DIHEN in ICP-SFMS was 1.02 into 10 to the power minus 18 gram per ml. So, you see what a small quantity of this radioactive substance 239Pu could be analyzed from 1 litre of urine by simply the enrichment factor and by taking into consideration the trace and the matrix separation, which could be done very efficiently, so that all other elements, which are in larger quantities can be separated out, and precisely, only the radioactive Pu can be analyzed. So, how was it done?

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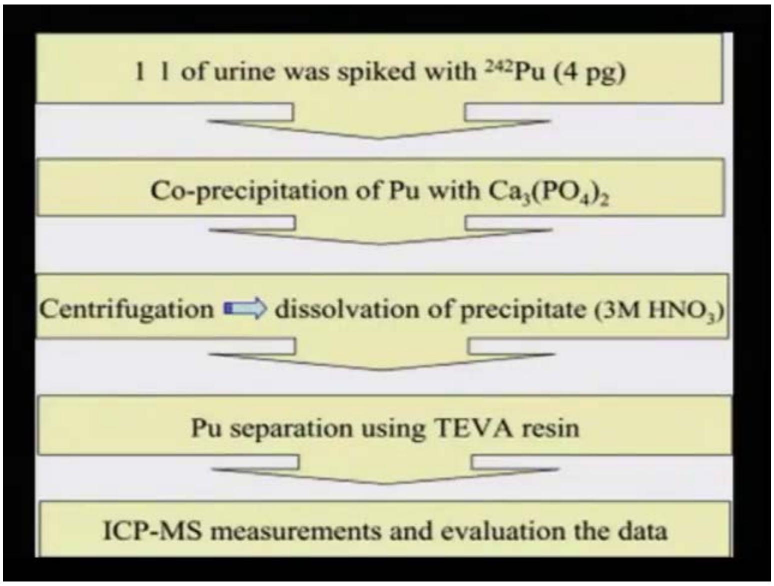

1 l of urine was spiked with ^{242}Pu (4 pg)

Co-precipitation of Pu with $Ca_3(PO_4)_2$

Centrifugation ⇨ dissolvation of precipitate (3M HNO_3)

Pu separation using TEVA resin

ICP-MS measurements and evaluation the data

Only 4 picogram of this 242 Pu was present and it was spiked into the urine. Co-precipitation of Pu with calcium phosphate was done. Then, centrifugation – dissolvation of the precipitate in 3 molar nitric acid was carried out. Pu separation took place and it was separated on a special resin called the TEVA resin (T E V A resin). And then, it was analyzed on ICP-MS, and the data was evaluated and it was found to be that it could be analyzed even in picogram per ml. And, starting from 1 litre of urine, it could be analyzed. So, there are not only such insistences, where urine samples or sea samples or very complex matrices are used as an analyte.

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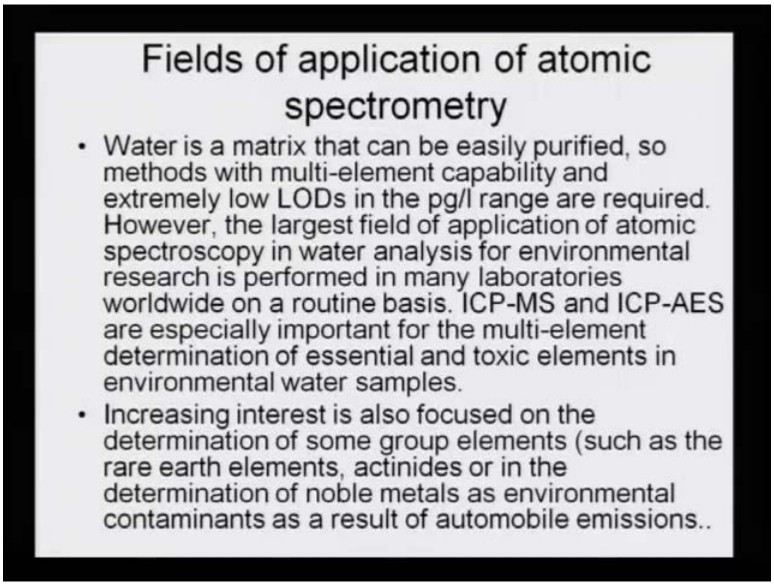

Fields of application of atomic spectrometry

- Water is a matrix that can be easily purified, so methods with multi-element capability and extremely low LODs in the pg/l range are required. However, the largest field of application of atomic spectroscopy in water analysis for environmental research is performed in many laboratories worldwide on a routine basis. ICP-MS and ICP-AES are especially important for the multi-element determination of essential and toxic elements in environmental water samples.
- Increasing interest is also focused on the determination of some group elements (such as the rare earth elements, actinides or in the determination of noble metals as environmental contaminants as a result of automobile emissions..

But, there are other fields of application of atomic spectrometry. Water is a matrix that can be easily purified. So, methods with multi-element capability and extremely low limits of detection in the picogram per litre range are required. However, the largest field of application of atomic spectroscopy is water analysis from environmental research and is performed in many laboratories worldwide on a routine basis. So, the most complex samples are the environmental samples, because they can have any kind of contaminant. It is not only metal, but metal-metal matrix complication and metal-non-metal also can create further more contamination. Now, in such a big complex matrix, to be able to specifically analyze, it is a big challenge. ICP-MS and ICP-AES are especially important for multi-element determination of essential and toxic elements in environmental water samples.

Increasing interest is also focused on the determination of some group elements, such as those of rare earth elements like actinides and lanthanide series and in the determination of noble metals as environmental contaminants as a result of automobile emission. So, you see the swear is very large. The working area can be from any source, any sample, complex or less complex, matrix being very contaminated or less contaminated, all can be analyzed for metal detection and metalloid detection so much, so that even the rare earth elements, which are in trace quantities or ultratrace quantities can also be detected by atomic spectrometry. The answer for such trace and ultratrace analysis is definitely ICP-MS or ICP-AES.

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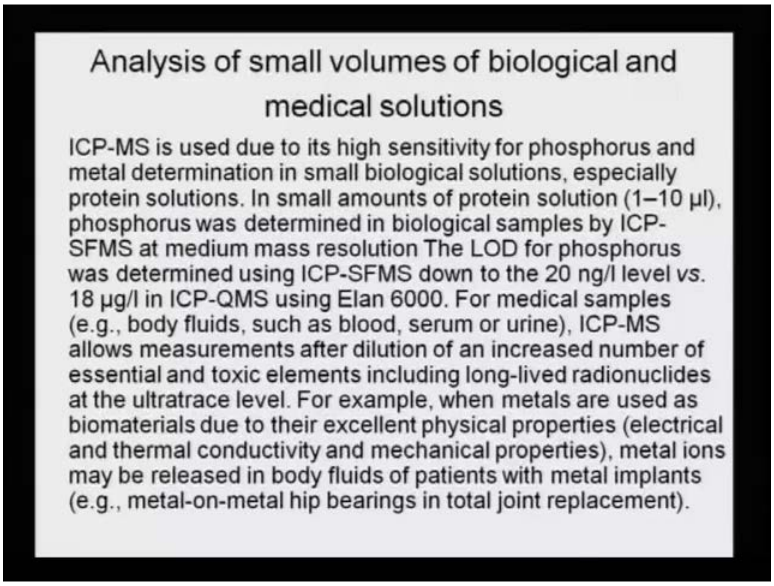

Analysis of small volumes of biological and medical solutions

ICP-MS is used due to its high sensitivity for phosphorus and metal determination in small biological solutions, especially protein solutions. In small amounts of protein solution (1–10 µl), phosphorus was determined in biological samples by ICP-SFMS at medium mass resolution The LOD for phosphorus was determined using ICP-SFMS down to the 20 ng/l level *vs.* 18 µg/l in ICP-QMS using Elan 6000. For medical samples (e.g., body fluids, such as blood, serum or urine), ICP-MS allows measurements after dilution of an increased number of essential and toxic elements including long-lived radionuclides at the ultratrace level. For example, when metals are used as biomaterials due to their excellent physical properties (electrical and thermal conductivity and mechanical properties), metal ions may be released in body fluids of patients with metal implants (e.g., metal-on-metal hip bearings in total joint replacement).

Analysis of small volumes of biological and medical solutions – now, you see that in biological systems as well as medical samples, the sample content or the analyte is in very small quantity. So, the answer is ICP-MS. ICP-MS is used due to its high sensitivity for phosphorus and metal determination in small biological solutions, especially protein solutions. In small amounts of protein solutions, that is, 1 to 10 microlitre, phosphorus was determined in biological samples by ICP-SFMS at medium mass resolution. The limit of detection for phosphorus was determined using ICP-SFMS down to 20 nanogram per litre level verses 18 microgram per litre in ICP-QMS using Elan 6000 machine. Now, you see that phosphorus content in these biological samples are as it is in either nanogram or microgram. And, they can be easily detected with the help of ICP-SFMS or with the help of ICP-QMS. If one needs to analyze in nanogram per litre, then ICP-SFMS is the answer. And, if the analyte is in microgram, ICP-QMS is the answer.

For medical samples, that is, body fluids, such as blood, serum, urine, these are the usual samples, which have to be analyzed for certain biological and medical solutions. ICP-MS allows measurements after dilution of an increased number of essential and toxic elements including long-lived radionuclides at the ultratrace levels. For example, when metals are used as biomaterials due to their excellent physical properties – electrical and thermal conductivity, and many mechanical properties – are taken into consideration, metal ions may be released in body fluids of patients with metal implants, that is, metal-on-metal hip bearings in total joint replacement. So, what happens is that it is not necessary the metal has come from any exterior source. It could also be that metal has been introduced as a hip joint replacement. Now, whether some metal is getting corroded and coming to the body fluids, such as blood or serum or urine also needs to be evaluated. And, for such things, it is possible to analyze these with the help of ICPs.

And also, sometimes, the body gets activated by or can absorb some long-lived radio nuclides. And, it is important to be able to analyze these dangerous isotopes of the metal, so that they can be eliminated or they could be a remedician technique for preserving or for removing these elements from the body.

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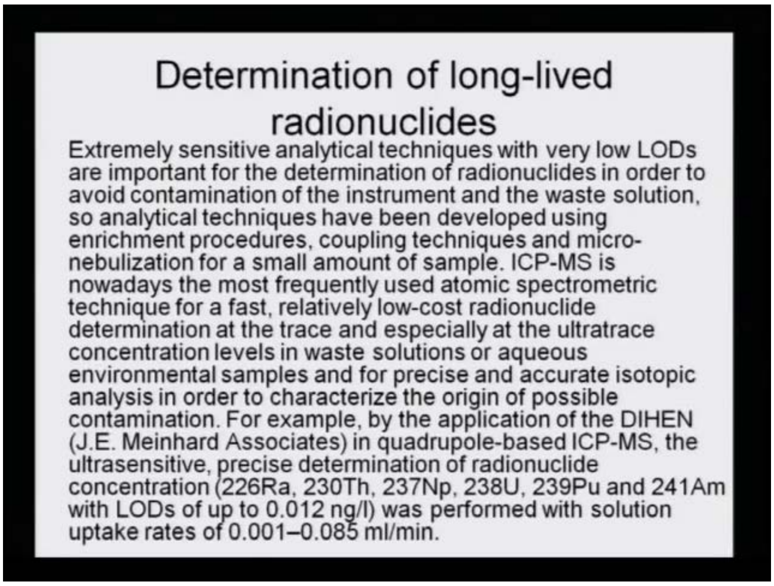

Determination of long-lived radionuclides

Extremely sensitive analytical techniques with very low LODs are important for the determination of radionuclides in order to avoid contamination of the instrument and the waste solution, so analytical techniques have been developed using enrichment procedures, coupling techniques and micro-nebulization for a small amount of sample. ICP-MS is nowadays the most frequently used atomic spectrometric technique for a fast, relatively low-cost radionuclide determination at the trace and especially at the ultratrace concentration levels in waste solutions or aqueous environmental samples and for precise and accurate isotopic analysis in order to characterize the origin of possible contamination. For example, by the application of the DIHEN (J.E. Meinhard Associates) in quadrupole-based ICP-MS, the ultrasensitive, precise determination of radionuclide concentration (226Ra, 230Th, 237Np, 238U, 239Pu and 241Am with LODs of up to 0.012 ng/l) was performed with solution uptake rates of 0.001–0.085 ml/min.

Determination of long-lived radionuclides – extremely sensitive analytical techniques with very low limits of detection are important for the determination of radionuclides in order to avoid contamination of the instrument and the waste solution. So, analytical techniques have to be developed using enrichment procedures, coupling techniques and micro-nebulization for a small amount of sample. Now, one thing has to be kept in mind that radionuclides are not like any other analytical element. Even their waste has to be properly disposed. And, the working of these and designing a method for the analysis of these long-lived radio nuclides is slightly different from the existing methods. That is why more precaution needs to be taken. It has to avoid contamination of the instrument. The instrument cannot remain with that nuclide. So, the proper washing and proper removal has to be kept in mind. And, the waste solution that is generated after the analysis also must be quite properly disposed. And, so, very small amount of sample should be taken and by the method of enrichment procedure coupled with a technique, which can do micro-nebulization. So, very small amount is going into the spray chamber of the ICP. That is the kind of the adjustment, so that only small amounts of samples are even taken into the machine.

The ICP-MS is nowadays the most frequently used atomic spectrometric method, which is a technique for fast, relatively low-cost radionuclide determination at the trace and especially at the ultratrace concentration levels in waste solutions or aqueous environmental samples and for precise and accurate isotopic analysis in order to characterize the origin of possible contamination. So, you see that these analytes are by themselves very special and, because of being very hazardous and they are long-lived radionuclide; that means they will keep on giving alpha, beta, gamma rays and will create more havoc. That is why their analytical method needs to be done in a much precise, and smaller analytical sample should be taken. And, this could be analyzed from all kinds of environmental samples and that is why this arrangement is slightly different from the methods that I had discussed so far. For example, by the application of DIHEN, that is, Meinhard Associates method in quadrupole-based ICP-MS, it was possible to analyze these. Now, this is a method, which has been specifically… DIHEN method is based on the co-workers name and they have used a quadrupole-based ICP-MS spectrometry.

The ultrasensitive, precise determination of the radionuclide concentration of 226Ra, 230 thorium, 237Np, 238 uranium, 239Pu and 241Am with very low limits of detection up to almost 0.12 nanogram per litre was performed with solution uptake rates of 0.001 to 0.085 ml per minute. You see the whole procedure has been modified and has been slowed down to such a micro-nebulizing flow that the intake itself of the sample is very small. And, if their uptake rates are as low as 0.001 to 0.085 ml microlitre per minute, you can imagine that the sample size is so small. And, they can be analyzed up to limit of detection is 0.01 to nanogram per litre. So, that small quantity of the radio nuclides, that is, 226 radium, 230 thorium, 237Np, 238 uranium, 239Pu and 241Am could be analyzed very effectively. So, with this, we have come to a situation, where I can say that trace and trace quantity analysis can be carried out in a very efficient manner. Similarly, there are other very specialized procedures for analyzing very special ceramic samples.

Here is a method that I would describe about the optimization or using an optimized microwave-assisted decomposition method for multi-element analysis of glass standard reference material and ancient glass specimens by ICP atomic emission spectrometry. This particular lecture I have dedicated for showing you that it is not only radio nuclides which can be analyzed by this method, but even samples from the ancient time, what was the elemental composition of a glass sample or a colored glass sample as compared to a multi-element glass standard? Where does it stand? How many elements are common? How many elements are different? What are the compositional changes in the ancient sample as well as in the modern samples of glass? How they have been modified? And, so on and so forth. An insight on the glass or the ceramic industry compositional changes can be understood by ICP-MS methods.

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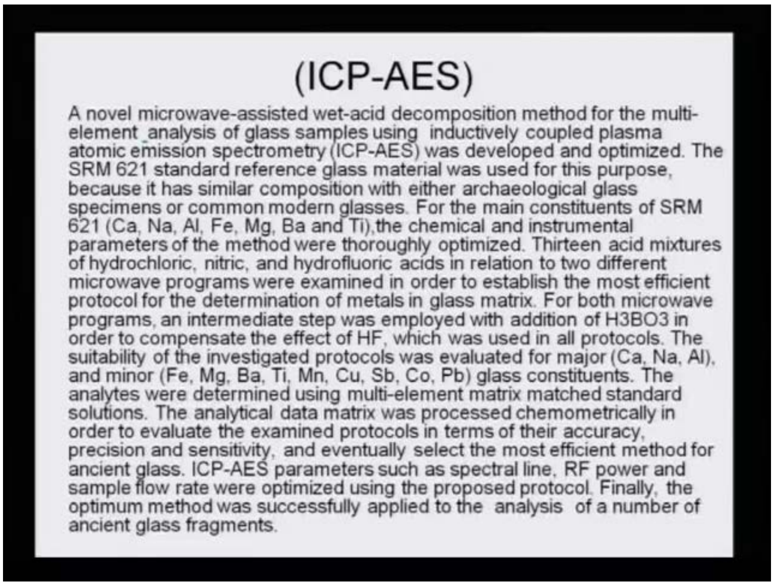

(ICP-AES)

A novel microwave-assisted wet-acid decomposition method for the multi-element analysis of glass samples using inductively coupled plasma atomic emission spectrometry (ICP-AES) was developed and optimized. The SRM 621 standard reference glass material was used for this purpose, because it has similar composition with either archaeological glass specimens or common modern glasses. For the main constituents of SRM 621 (Ca, Na, Al, Fe, Mg, Ba and Ti),the chemical and instrumental parameters of the method were thoroughly optimized. Thirteen acid mixtures of hydrochloric, nitric, and hydrofluoric acids in relation to two different microwave programs were examined in order to establish the most efficient protocol for the determination of metals in glass matrix. For both microwave programs, an intermediate step was employed with addition of H3BO3 in order to compensate the effect of HF, which was used in all protocols. The suitability of the investigated protocols was evaluated for major (Ca, Na, Al), and minor (Fe, Mg, Ba, Ti, Mn, Cu, Sb, Co, Pb) glass constituents. The analytes were determined using multi-element matrix matched standard solutions. The analytical data matrix was processed chemometrically in order to evaluate the examined protocols in terms of their accuracy, precision and sensitivity, and eventually select the most efficient method for ancient glass. ICP-AES parameters such as spectral line, RF power and sample flow rate were optimized using the proposed protocol. Finally, the optimum method was successfully applied to the analysis of a number of ancient glass fragments.

ICP-AES is the answer for analytical method for the glass analysis. A novel microwave-assisted wet-acid decomposition method for the multi-element analysis of glass samples using inductively coupled plasma atomic emission spectrometry, that is, ICP-AES was developed and optimized. Now, you see that in this particular method, there is a special emphasis on use of microwave-assisted acid digestion. Why? Because glass is basically made up of silicates and it is very difficult to normally digest the silicates by the normal sulphuric acid and nitric acid and hydrochloric acid. And, the normal digestion processes do not break the matrix of the silicates. And, unless and until the matrix of the silicate is broken down, the metals that are embedded inside the matrix cannot be extracted or digested. That is why a programmed microwave-assisted wet acid decomposition is a must for glass samples.

The SRM 261 standard reference glass material was used for this purpose, because it has similar composition with either archaeological glass specimens or common modern glasses. So, as I told you, there needs to be a reference. Now, reference standard of glass, which is commonly used is SRM 621, was taken into consideration for this analytical comparison. And then, compared with the modern glasses that are being produced in today’s technologically advanced glass industry; or, archaeological samples from the ancient times are also compared.

The main constituents of SRM 621 are calcium, sodium, aluminum, iron, magnesium, barium and titanium. The chemical and instrumental parameters of the method were thoroughly optimized. 13 acid mixtures of hydrochloric acid, nitric acid and hydrofluoric acid in order to establish the most efficient protocol for the determination of metals in glass matrix was carried out. Now, the beauty of microwave is that it can use a variety of acids in a sequential manner. And, to be able to break the silicate mesh work, the hydrofluoric acid is the only answer. And, that is why a beautifully programmed method using hydrochloric acid, that is, HCl, nitric acid, that is, HNO3 and hydrofluoric acid, which is HF was used, so that completely wet digestion of the matrix can be brought about. For both microwave programs, an intermediate step was employed with an addition of boric acid, also, in order to compensate the effect of the hydrofluoric acid, which was used in all protocols. The suitability of the investigated protocol was evaluated for major elements calcium, sodium, aluminum, and then, the minor quantities that are iron, magnesium, barium, titanium, manganese, copper, antimony, cobalt and led in the glass major constituents. So, we understand that this is one of the best methods of designing the microwave wet digestion.

Three things have to be kept in mind, that when we are analyzing the glass samples, particularly, glass sample of the type SRM 621, which is a multi-element composite and which is embedded in the silicates, it needs to have a proper microwave digestion programming. 13 acid mixtures of hydrochloric acid, nitric acid and hydrofluoric acid mixtures have been utilized. To be able to completely digest the samples for all the metal contents, such as, calcium, sodium, aluminum as major components, and in minor components, iron, magnesium, barium, titanium, manganese, copper, antimony, cobalt and led. The analytes were determined using multi-element matrix matched standard solution. Obviously, it is always a calibration method. So, the standard also must have all these components to be able to analyze the same metals in the sample.

The analytical data matrix was processed chemometrically in order to evaluate the examined protocols in terms of their accuracy, precision and sensitivity, and eventually, select the most efficient method for the ancient glass. So, there was some permutation and combination in the method that was developed. And, the best method that gave the best analytical data in terms of its chemometric manipulation was the one which was used for analysis of the ancient glass samples or the archeological samples.

ICP-AES parameters such as spectral line, RF power and sample flow rate were optimized using the proposed protocols, which were used in the process. So, these are the three things, which were manipulated – the spectral lines; that means, which line to choose. The other day, I was mentioning when I was talking about ICP and AAS, I said that in ICP, we can do multi-element analysis. And, while we are doing multi-element analysis, if the two metals have very close spectral lines, then we choose the second grade of the spectral lines for the second element, so that there is no interferences caused by the spectral lines and there should not be any confusion, because the two metals may not be able to be discriminated properly. Finally, the optimal method was successfully applied to the analysis of a number of ancient glass fragments. To be able to know what the glass composition was at that time or what was there methodology to prepare these very different types of glass material, which are compared with the modern glass, one needs to understand the composition of these in terms of their metal content.

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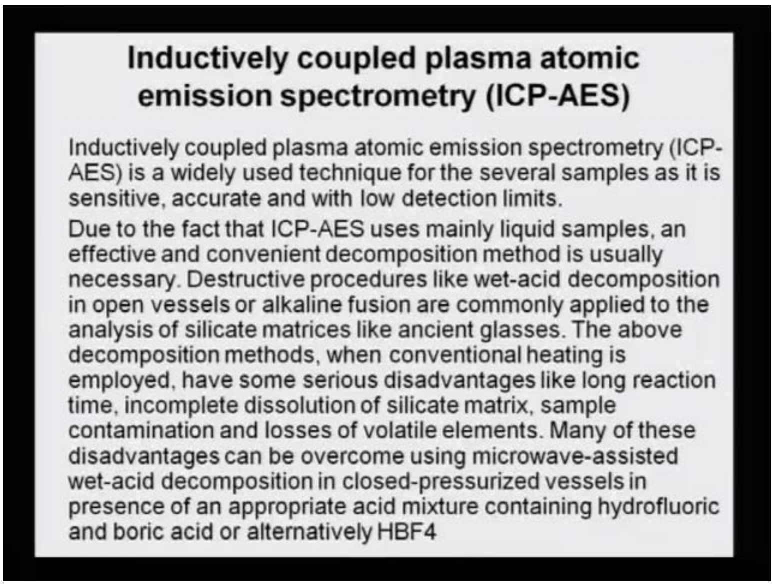

Inductively coupled plasma atomic emission spectrometry (ICP-AES)

Inductively coupled plasma atomic emission spectrometry (ICP-AES) is a widely used technique for the several samples as it is sensitive, accurate and with low detection limits.

Due to the fact that ICP-AES uses mainly liquid samples, an effective and convenient decomposition method is usually necessary. Destructive procedures like wet-acid decomposition in open vessels or alkaline fusion are commonly applied to the analysis of silicate matrices like ancient glasses. The above decomposition methods, when conventional heating is employed, have some serious disadvantages like long reaction time, incomplete dissolution of silicate matrix, sample contamination and losses of volatile elements. Many of these disadvantages can be overcome using microwave-assisted wet-acid decomposition in closed-pressurized vessels in presence of an appropriate acid mixture containing hydrofluoric and boric acid or alternatively HBF_4

Inductively coupled plasma atomic emission spectrometry – again and again, I am telling about these machines in so much of great details, because one analyzer should be able to discriminate what to use and where to use. Inductively coupled plasma atomic emission spectrometry, that is, ICP-AES is a widely used technique for the several samples as it is sensitive, accurate and with low limits of detection.

Due to the fact that ICP-AES uses mainly liquid samples, an effective and convenient decomposition method is usually necessary. Now, we know that this is a method which can be used for any and every sample although it is sensitive and accurate and goes up to lower limits of detection. Therefore, the only challenge that an analyzer or an analyst has to face is to be able to prepare the liquid sample most effectively and most conveniently. If the decomposition or digestion step is very cumbersome or long drawn, then it is not a very good technique and cannot be adopted by every laboratory. Hence, the decomposition method should be very efficient. And, that is the most important step, because as I told you, silicate or glass samples are very tough to digest. And, unless and until there is a complete wet digestion of these glass silicates, it is not possible to get all the metals extracted into the solution. And, unless and until all the metals come into the solution, the analysis can never be exhausted and complete.

Destructive processes like wet acid decomposition in open vessels or alkaline fusion are commonly applied to analysis of silicate matrices like ancient glasses. The above decomposition methods, when conventional heating is employed, have some very serious disadvantages like long reaction time, incomplete dissolution of silicate matrix, sample contamination and losses of volatile elements. Many of these disadvantages can be overcome using microwave-assisted wet-acid decomposition in closed-pressurized vessel in presence of an appropriate acid mixture containing hydrofluoric and boric acid or alternatively HBF4, that is, the hydrofluoro boro acid. So, you see that what the disadvantages are if we try to digest these glass samples in open vessels.

There are several and very serious disadvantages. That is, firstly, it is a very long process and it may or may not completely digest the silicate. And, as what I told you, if the silicate matrix does not get completely digested, the metals that are embedded in side, which are much smaller in quantities or even in sometimes trace quantities, cannot be extracted or digested into the solution. And, unless and until they come into the solution, it is not possible to analyze them by ICP-AES, and the sample in the open vessel may get contaminated by outside agencies. And, sometimes, the volatile elements also may be lost, because there is an open vessel and it is getting heated, and the volatile elements can go away from the matrix or from the dissolved solution. So, that is why it was important to design a method of microwave-assisted wet-acid decomposition, because it is carried out in pressurized Teflon vessels. And therefore, because it is made up of Teflon, it does not get affected by any of these acids like hydrochloric acid, nitric acid, boric acid or even hydrofluoric acid. And, sometimes, the combination of boric acid and hydrofluoric acid has also been taken into account for the complete dissolution of the silicate matrix.

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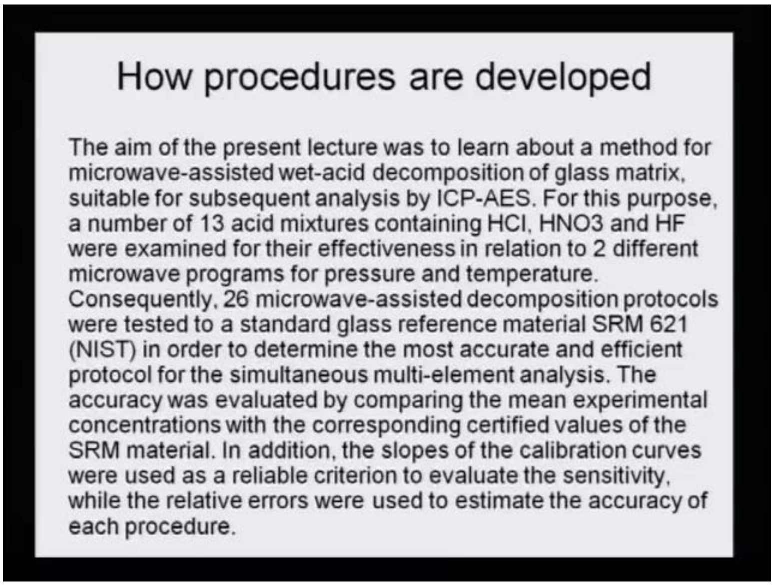

How procedures are developed

The aim of the present lecture was to learn about a method for microwave-assisted wet-acid decomposition of glass matrix, suitable for subsequent analysis by ICP-AES. For this purpose, a number of 13 acid mixtures containing HCl, HNO3 and HF were examined for their effectiveness in relation to 2 different microwave programs for pressure and temperature. Consequently, 26 microwave-assisted decomposition protocols were tested to a standard glass reference material SRM 621 (NIST) in order to determine the most accurate and efficient protocol for the simultaneous multi-element analysis. The accuracy was evaluated by comparing the mean experimental concentrations with the corresponding certified values of the SRM material. In addition, the slopes of the calibration curves were used as a reliable criterion to evaluate the sensitivity, while the relative errors were used to estimate the accuracy of each procedure.

How procedures are developed? See there is always… I have told time and again that there is a necessity. And, for this necessity, there is a new invention. So, similarly, that is how science progresses. When there is no need, there is no science, because everything works on what has been already invented. But, every time there is a new type of sample, a new type of matrix and it is felt that complete digestion has not taken place by the existing method, and the new method is developed. The aim of present lecture was to learn about a method for microwave-assisted wet-acid decomposition of the glass matrix suitable for subsequent analysis by ICP-AES. It was felt that glass, which is the toughest to digest needs more attention, and therefore, there should be a new method of microwave-assisted wet-acid decomposition. For this purpose, a number of 13 acid mixtures containing HCl, HNO3 and HF were examined for their effectiveness in relation to two different microwave programs for pressure and temperature. So, the design of the method of microwave is now elaborated. You will see that two different programs were conducted in microwave analysis just the way we have cooking recipes; we cook dhal in many ways; and, the sambar is made in another way; and, some other amty is made in a third way. Similarly, we have microwave-assisted programmed techniques for digestion, so that we see which one is better. In the case of food, it is the taste, which matters, but in this case, it is the best dissolution of all the components, which matters. I am giving you this day-to-day life example only to be able to correlate, although dhal has nothing to do with microwave digestion of silicates samples.

Consequently, 26 microwave-assisted composition protocols were tested to a standard glass reference material, that is, SRM 621, and this was listed in the NIST library in order to determine the most accurate and efficient protocol for the simultaneous multi-element analysis. The accuracy was evaluated by comparing the mean experimental concentrations with the corresponding certified values of the SRM material. So, repeatedly, the different protocols were applied, different methods of microwave acid digestions were applied, and it was found that, out of these methods, which are the methods, which give consistent result, because the standard reference glass sample SRM 621, has a very finite composition. And, so, that is taken as a reference standard. So, the first analytical protocol was tested against this SRM 621 glass sample, and then, it was used as a reference standard for calibration method for the glass samples. In addition, the slopes of the calibration curves were used as a reliable criterion to evaluate the sensitivity, while the relative errors were used to estimate the accuracy of each procedure. So, the whole method was developed. It was a calibration method, which was then used for the new samples – whether it is archeological sample or whether it is modern glass sample, were all compared with the reference sample SRM 621.

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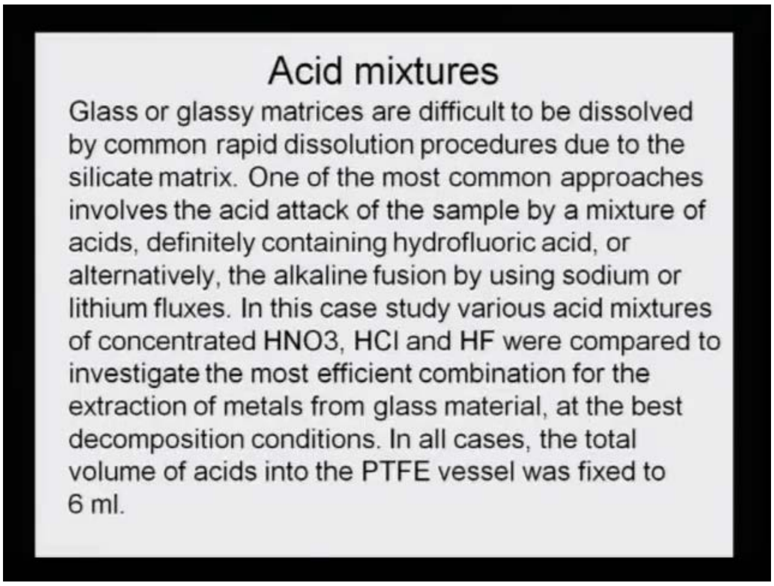

Acid mixtures

Glass or glassy matrices are difficult to be dissolved by common rapid dissolution procedures due to the silicate matrix. One of the most common approaches involves the acid attack of the sample by a mixture of acids, definitely containing hydrofluoric acid, or alternatively, the alkaline fusion by using sodium or lithium fluxes. In this case study various acid mixtures of concentrated HNO3, HCl and HF were compared to investigate the most efficient combination for the extraction of metals from glass material, at the best decomposition conditions. In all cases, the total volume of acids into the PTFE vessel was fixed to 6 ml.

Acid mixtures – why there is a necessity for having such combination of acid mixtures? Glass and glassy matrices are difficult to be dissolved by common rapid dissolution processes due to the silicate matrix. Now, if we have suppose a metal or an alloy, it is very easy to digest in an open vessel simply by adding a little hot dilute nitric acid or hot dilute HCl. And, the metal will completely come into the solution by acid digestion by merely heating little bit. But, that is not the story when we are analyzing silicate matrices or glass sample. Why? Because they have a very complicated structure and a very tightly bound structure.

One of the most common approaches involving acid attack of the sample by a mixture of acids, definitely containing hydrofluoric acid, or alternatively, the alkaline fusion by using sodium or lithium fluxes was carried out. Now, there have been methods, which you may have come across in your BSc and MSc experiments that metals were analyzed or certain compounds were analyzed by sodium fusion. In place of sodium, even lithium fusion can be taken. That means a compound and a piece of sodium are kept side by side and then it is ignited. In the burning process of the sodium fusion, this gets into solution. And, when water is added to this whole charged material, it is expected that all of it will come into the solution form. But, that was not a very convenient method. That is why the use of hydrofluoric acid was introduced. In this case study, various acid mixtures of concentrated nitric acid, hydrochloric acid and hydrofluoric acid, were compared to investigate the most efficient combination for the extraction of metals from glass material. So, first, a comparative data was created by using only hydrochloric acid, the traditional digestion acid or by using nitric acid, which is also traditionally used or conventionally used for digestion of matrix.

But, it was found that not all the metal came into solution, and that is why, there was an introduction of hydrofluoric acid. But, the problem of using hydrofluoric acid is that it cannot be used in glass beakers, because glasses are again made up of silicate, and silicates react with hydrofluoric acid. So, then, what will happen? That it will digest the beaker also and the sample also. That is why these Teflon vessels were brought into picture. And, when it was investigated and found that which one is the most efficient combination of extraction, it was found that the best decomposition conditions were when all the three are used together. In all cases, the total volume of acids in these Teflon (PTFE) vessels was fixed to 6 ml. It cannot exceed more than 6 ml, because the vessels are slightly big, but there has to be a vacuum space to be able to handle the pressures of the gas that are generated out of these acids; they are all not in liquid form, some of them are also in the vapor form. And, if the liquid volume large, then the total space that would be left will be small.

So, that was kept in mind that these three acids, that is, the hydrochloric acid, the nitric acid and the hydrofluoric acid, must be taken in combination. First thing, for the glass analysis or decomposition and also, the total volume of these three acids, concentrated acids, should not exceed more than 6 ml volume.

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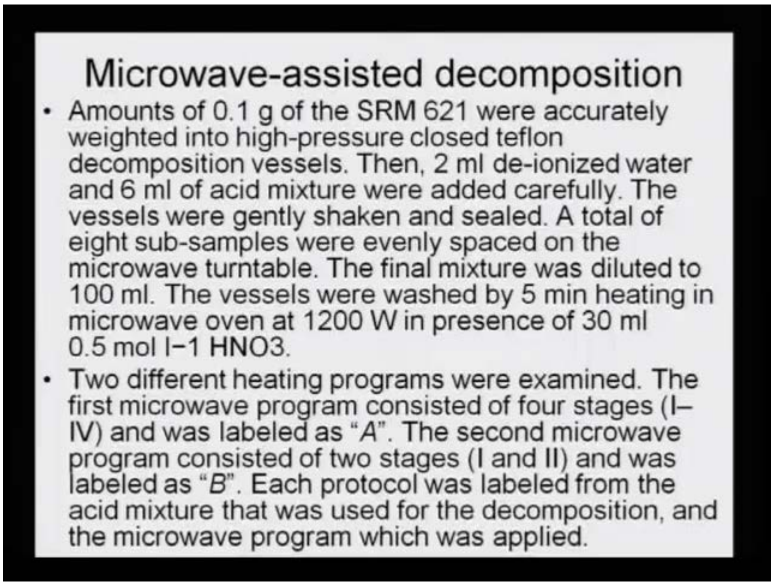

Microwave-assisted decomposition

- Amounts of 0.1 g of the SRM 621 were accurately weighted into high-pressure closed teflon decomposition vessels. Then, 2 ml de-ionized water and 6 ml of acid mixture were added carefully. The vessels were gently shaken and sealed. A total of eight sub-samples were evenly spaced on the microwave turntable. The final mixture was diluted to 100 ml. The vessels were washed by 5 min heating in microwave oven at 1200 W in presence of 30 ml 0.5 mol l−1 HNO_3.
- Two different heating programs were examined. The first microwave program consisted of four stages (I–IV) and was labeled as "*A*". The second microwave program consisted of two stages (I and II) and was labeled as "*B*". Each protocol was labeled from the acid mixture that was used for the decomposition, and the microwave program which was applied.

Microwave-assisted decomposition – amounts of 0.1 gram of the standard SRM 621 were accurately weighed into high pressure closed Teflon decomposition vessels. Then, 2 ml of de-ionized water and 6 ml of acid mixtures were added carefully. The vessels were gently shaken and sealed. A total of 8 sub-samples were evenly spaced on the microwave turntable. The microwave can hold 8 such vessels, and in all the 8 vessels, there should be at least water or the samples dissolved in water. The turn table will not work if all the vessels are not fitted. And, to have an efficient absorption of microwave and no wastage of microwave energy being taken place, all these 8 Teflon vessels, which are on a turntable in a microwave should have water or the sample, which is digested with acids and water, because microwave energy only excites the water molecule, and that is how it helps in digestion. The final mixture was diluted to 100 ml. After the digestion had taken place, we can then increase the volume to 100 ml. The vessels were washed by 5 minutes heating in microwave at 1200 wattage in presence of 30 ml of 0.5 molar solution of nitric acid.

Two different heating programs were examined. The first microwave program consisted of four stages of 1 to 4 and was labeled as A method. The second microwave program consisted of two stages (1 and 2) and was labeled as B method. Each protocol was labeled from the acid mixture that was used for the decomposition, and the microwave program which was applied. So, two different programs were carried out as what I mentioned in the earlier slide, and it was compared which method – whether the method with four steps or the method B with just two steps, which one is better for the complete digestion of this standard reference glass sample?

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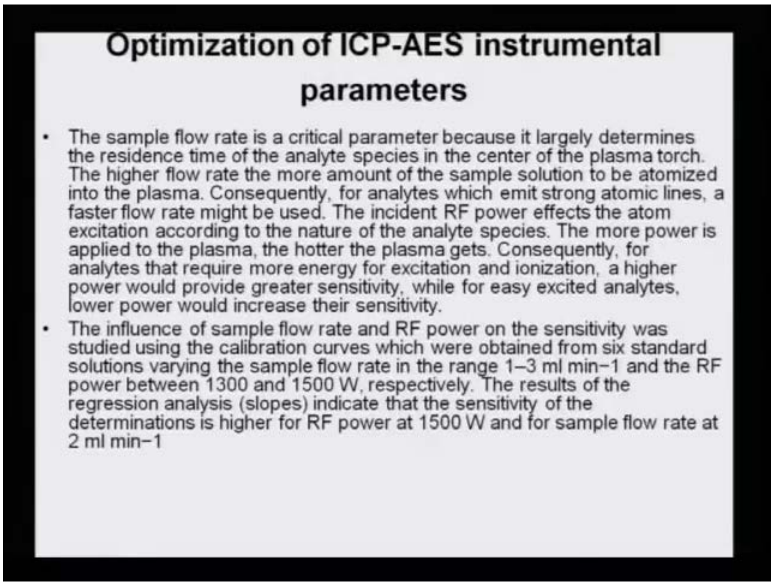

Optimization of ICP-AES instrumental parameters

- The sample flow rate is a critical parameter because it largely determines the residence time of the analyte species in the center of the plasma torch. The higher flow rate the more amount of the sample solution to be atomized into the plasma. Consequently, for analytes which emit strong atomic lines, a faster flow rate might be used. The incident RF power effects the atom excitation according to the nature of the analyte species. The more power is applied to the plasma, the hotter the plasma gets. Consequently, for analytes that require more energy for excitation and ionization, a higher power would provide greater sensitivity, while for easy excited analytes, lower power would increase their sensitivity.
- The influence of sample flow rate and RF power on the sensitivity was studied using the calibration curves which were obtained from six standard solutions varying the sample flow rate in the range 1–3 ml min−1 and the RF power between 1300 and 1500 W, respectively. The results of the regression analysis (slopes) indicate that the sensitivity of the determinations is higher for RF power at 1500 W and for sample flow rate at 2 ml min−1

Optimization of ICP-AES instrumental program – the sample flow rate is a critical parameter because it largely determines the residence time of the analyte species in center of the plasma torch. The higher flow rate the more amount of sample solution to be atomized into the plasma. Consequently, the analytes, which emit strong atomic lines, a fast flow rate might be used. The incident RF power effects the atom excitation according to the nature of the analyte species. The more power is applied to the plasma, the hotter the plasma gets. Consequently, for analytes that require more energy for excitation and ionization, a high power would provide greater sensitivity, while the easy excited analytes at lower power would increase their sensitivity. So, here, there has to be certain instrumentational manipulation also. I just told you the sample preparation needs manipulation and complete digestion. Similarly, there has to be some parameters that need to be adjusted according to the sensitivity and the presence at which they are in the solution while analyzing on ICP-AES, and what are these parameters? The incident RF power that effects the atom excitation will also depend on the nature of the analyte species. More power will be applied for plasma to get hotter, so that more energy can be provided for excitation and ionization, and greater sensitivity can be attained.

The influence of sample flow rate and RF power on sensitivity was studied using calibration curves, which were obtained from 6 standard solutions varying the sample flow rate in the range of 1 to 3 ml per minute and the RF power between 1300 to 1500 watt, respectively. The results of the regression analysis, that is, the slopes indicate that the sensitivity of the determination is higher for RF power at 1500 wattage, and for sample flow rate at 2 ml per minute is the optimal. So, these kind of optimization studies need to be carried out to be able to find out. It not that only one method is designed and the new experiment is carried out on that one method. And, it is found that this is the foolproof method; nobody can say that this is the best method unless there is an optimization. When we try to analyze, we need to carry out several methods, and from those several new methods, then the best method is chosen to be used on a routine basis.

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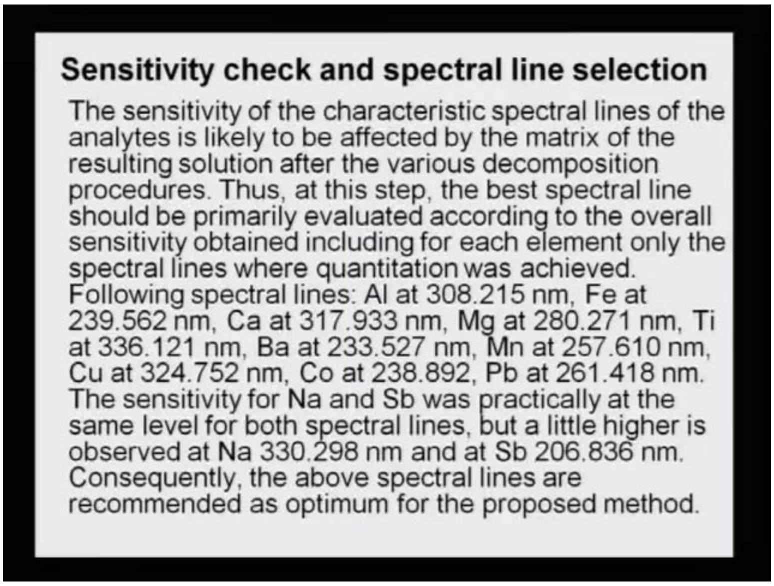

Sensitivity check and spectral line selection

The sensitivity of the characteristic spectral lines of the analytes is likely to be affected by the matrix of the resulting solution after the various decomposition procedures. Thus, at this step, the best spectral line should be primarily evaluated according to the overall sensitivity obtained including for each element only the spectral lines where quantitation was achieved. Following spectral lines: Al at 308.215 nm, Fe at 239.562 nm, Ca at 317.933 nm, Mg at 280.271 nm, Ti at 336.121 nm, Ba at 233.527 nm, Mn at 257.610 nm, Cu at 324.752 nm, Co at 238.892, Pb at 261.418 nm. The sensitivity for Na and Sb was practically at the same level for both spectral lines, but a little higher is observed at Na 330.298 nm and at Sb 206.836 nm. Consequently, the above spectral lines are recommended as optimum for the proposed method.

Sensitivity check and spectral line selection – I have been talking about spectral line selection only when we are discussing ICP. I said that if two elements have close spectral lines, it will not be able to determine whether it belongs to element A or whether it belongs to element B. In such a case, the element A is chosen as it is, and for the element

B, another spectral line away from it should be chosen, so that there are no spectral line interferences. The sensitivity of a characteristic spectral line of the analyte is likely to affect by the matrix of the resulting solution after various decomposition procedures. So, what happens – when different acids are added, the sensitivity also changes; it does not remain the same. Now, under the given compositional changes because there are also these acids, which are in the solution form, there has to be some other manipulation in terms of selection of the spectral lines. Thus, at this step, the best spectral line should be primarily evaluated according to the overall sensitivity obtained including for each element only the spectral line where quantitation was achieved. So, that means that whichever spectral line represents that particular element highly, that should be chosen. So, here again, there are some manipulations that need to be done for such a program and complicated analysis of glass samples.

Following spectral lines, such as for aluminum, 308.215 nanometer was chosen; for iron, it was at 239.521 nanometer; for calcium, it was at 317.933 nanometer; for magnesium, 280.271 nanometer; for titanium, it was chosen at 336.121 nanometer; for cobalt, it was at 238.892 nanometer; for lead, it was at 261.418 nanometer. Now, you see they are fairly between the range of 308 to 261 and 233; different spectral lines for different elements were specifically chosen. The sensitivity for sodium and antimony was practically at the same level for both spectral lines, but a little higher is observed at sodium 330.298 nanometer, and for antimony, it was 206.836 nanometer. So, that is why since they were very close originally, two different lines were chosen for sodium and antimony, so that they can be separated out, and there should not be any confusion whether this line and this concentration belongs to sodium or antimony. Consequently, the above spectral lines were recommended as an optimum proposed method. So, this was finally, concluded that aluminum at 308, iron at 239, calcium at 317, magnesium at 280, titanium at 336, barium at 233, manganese at 257, copper at 324, cobalt at 238, lead at 261, and for sodium – 330, and antimony – 206 were the final chosen spectral lines for this glass analysis.

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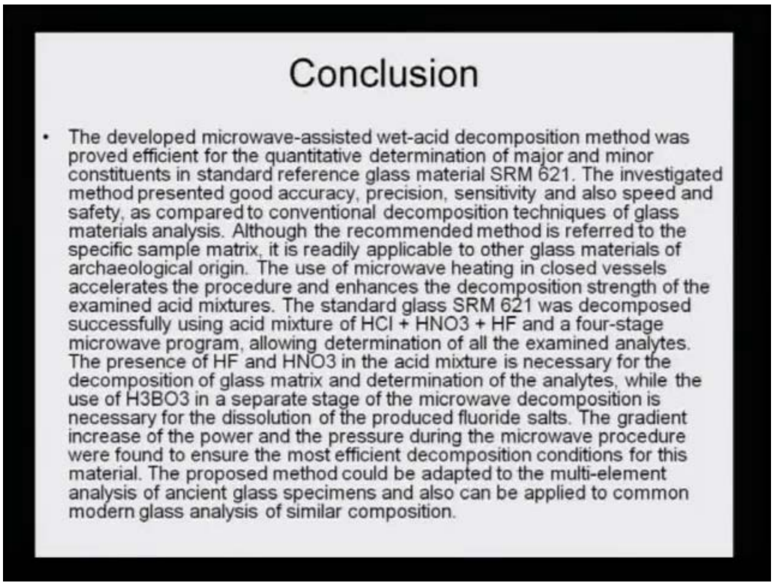

Conclusion

- The developed microwave-assisted wet-acid decomposition method was proved efficient for the quantitative determination of major and minor constituents in standard reference glass material SRM 621. The investigated method presented good accuracy, precision, sensitivity and also speed and safety, as compared to conventional decomposition techniques of glass materials analysis. Although the recommended method is referred to the specific sample matrix, it is readily applicable to other glass materials of archaeological origin. The use of microwave heating in closed vessels accelerates the procedure and enhances the decomposition strength of the examined acid mixtures. The standard glass SRM 621 was decomposed successfully using acid mixture of $HCl + HNO_3 + HF$ and a four-stage microwave program, allowing determination of all the examined analytes. The presence of HF and HNO_3 in the acid mixture is necessary for the decomposition of glass matrix and determination of the analytes, while the use of H_3BO_3 in a separate stage of the microwave decomposition is necessary for the dissolution of the produced fluoride salts. The gradient increase of the power and the pressure during the microwave procedure were found to ensure the most efficient decomposition conditions for this material. The proposed method could be adapted to the multi-element analysis of ancient glass specimens and also can be applied to common modern glass analysis of similar composition.

Conclusion – the developed microwave-assisted wet-acid decomposition method was proven to be most efficient for the quantitative determination of major and minor constituents in standard reference glass material SRM 621. The investigated method presented good accuracy, precision, sensitivity and also speed and safety, as compared to conventional decomposition techniques of glass material analysis. Although the recommended method is referred to as specific sample matrix, it is readily applicable to other glass materials of archaeological origin. That means it is a method which is not only for reference sample, but it is also meant for modern glass samples and old time ancient glass samples. So, it is a method for all types of glass samples; complicated and very intricate analytical method has been developed.

The use of microwave heating in closed vessels accelerates the procedure and enhances the decomposition strength of the examined acid mixtures. The standard glass SRM 621 was decomposed successfully using acid mixtures – hydrochloric acid, nitric acid and hydrofluoric acid, and a four stage microwave program, allowing determination of all the examined analytes was carried out. The presence of hydrofluoric acids and nitric acid in the acid mixture is necessary for the decomposition of glass matrix as what I mentioned. Again and again, I am mentioning because silicates are very tough to analyze and to decompose. And, determination of the analytes was carried out while the use of hydro boric acid in a separate stage of the microwave decomposition is necessary for the dissolution of the produced fluoride salts. So, first, it converts into the… When it is reacted with HF, it converts in to fluoride, and then, the boric acid further dissolves the fluorides. The gradient increase of the power and the pressure during the microwave procedure were found to ensure the most efficient decomposition conditions for this material. The proposed method could be adapted for a multi-element analysis of ancient glass specimens and also can be applied to common modern glass analysis of similar composition. So, it is a method which has been found to be foolproof for all types of glass samples.

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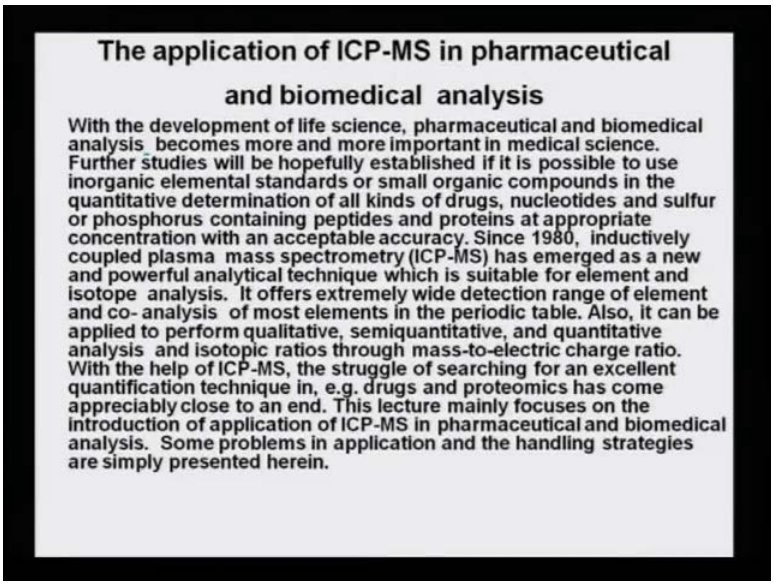

The application of ICP-MS in pharmaceutical and biomedical analysis

With the development of life science, pharmaceutical and biomedical analysis becomes more and more important in medical science. Further studies will be hopefully established if it is possible to use inorganic elemental standards or small organic compounds in the quantitative determination of all kinds of drugs, nucleotides and sulfur or phosphorus containing peptides and proteins at appropriate concentration with an acceptable accuracy. Since 1980, inductively coupled plasma mass spectrometry (ICP-MS) has emerged as a new and powerful analytical technique which is suitable for element and isotope analysis. It offers extremely wide detection range of element and co- analysis of most elements in the periodic table. Also, it can be applied to perform qualitative, semiquantitative, and quantitative analysis and isotopic ratios through mass-to-electric charge ratio. With the help of ICP-MS, the struggle of searching for an excellent quantification technique in, e.g. drugs and proteomics has come appreciably close to an end. This lecture mainly focuses on the introduction of application of ICP-MS in pharmaceutical and biomedical analysis. Some problems in application and the handling strategies are simply presented herein.

Then, coming to the use of ICP in pharmaceutical and biomedical analysis, as I said, every time, there is a new type of sample, which has complicated matrix; there is a challenge for the analyst to design a method, which should extract all the ingredients, and therefore, only the efficient analysis or data can be obtained. With the development of life sciences, pharmaceuticals and biomedical analysis, it becomes more and more important in medical science to be able to utilize these techniques and to analyze the analyte. Further studies will be hopefully established if it is possible to use inorganic elemental standards or small organic compounds in the inorganic standards and quantitatively be able to determine all the kinds of drugs, nucleotides and sulfur or phosphorus containing peptides and proteins at appropriate concentration with an acceptable accuracy. Since 1980, inductively coupled plasma mass spectrometry, that is, ICP-MS has emerged as a new and powerful analytical technique, which is suitable for elements and isotope analysis. It offers extremely wide detection range of elements and co-analysis of most elements in the periodic table. Also, it can be applied to perform qualitative, semiquantitative, and quantitative analysis and isotopic ratios through mass-to-electric charge ratio, that is, with the help of the MS.

With the help of ICP-MS, the struggle of searching for an excellent quantification technique in that example like drugs and proteomics has become appreciably close to an end. This lecture mainly focuses on the introduction of the application of ICP-MS in pharmaceutical and biological analysis method. Some problems in application and handling strategies are simply presented here. So, how this ICP and the ICP-MS can be efficiently used for pharma samples or biomedical samples? What are the manipulations that required to be done? You know the basic working of ICP and the ICP-MS, but there are just the way we saw for glass samples, some digestion methods had to be a new method. Similarly, how to handle these type of samples? We will take a look at it.

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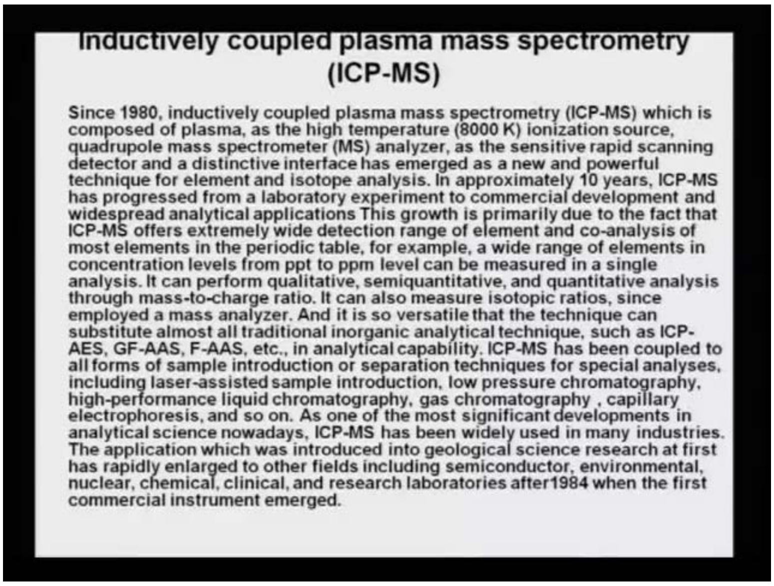

Inductively coupled plasma mass spectrometry (ICP-MS)

Since 1980, inductively coupled plasma mass spectrometry (ICP-MS) which is composed of plasma, as the high temperature (8000 K) ionization source, quadrupole mass spectrometer (MS) analyzer, as the sensitive rapid scanning detector and a distinctive interface has emerged as a new and powerful technique for element and isotope analysis. In approximately 10 years, ICP-MS has progressed from a laboratory experiment to commercial development and widespread analytical applications This growth is primarily due to the fact that ICP-MS offers extremely wide detection range of element and co-analysis of most elements in the periodic table, for example, a wide range of elements in concentration levels from ppt to ppm level can be measured in a single analysis. It can perform qualitative, semiquantitative, and quantitative analysis through mass-to-charge ratio. It can also measure isotopic ratios, since employed a mass analyzer. And it is so versatile that the technique can substitute almost all traditional inorganic analytical technique, such as ICP-AES, GF-AAS, F-AAS, etc., in analytical capability. ICP-MS has been coupled to all forms of sample introduction or separation techniques for special analyses, including laser-assisted sample introduction, low pressure chromatography, high-performance liquid chromatography, gas chromatography , capillary electrophoresis, and so on. As one of the most significant developments in analytical science nowadays, ICP-MS has been widely used in many industries. The application which was introduced into geological science research at first has rapidly enlarged to other fields including semiconductor, environmental, nuclear, chemical, clinical, and research laboratories after1984 when the first commercial instrument emerged.

Inductively coupled plasma mass spectrometry – since 1980, inductively coupled plasma mass spectrometry, that is, ICP-MS, which is composed of plasma, as a high temperature (8000 kelvin) ionization source with the quadrupole mass spectrometer analyzer, as the sensitive rapid scanning detector and a distinctive interface has emerged as a new and powerful technique for element and isotope analysis. In approximately 10 years time, ICP-MS has progressed from a laboratory experiment to commercial development and widespread analytical applications. So, you see over a period of time, it has become so popular. This growth is primarily due to fact that ICP-MS offers extremely wide detection range of element and co-analysis of most elements in the periodic table. For example, a wide range of elements in the concentration levels from ppt to ppm level can be measured in a single analysis. So, whether it is a parts per trillion or whether it is parts per million, at every range, ICP-MS can be used. It can perform qualitative, semiquantitative and quantitative analysis through the mass-to-charge ratio. That means if we want to find out whether it is present or not any element, or in what kind of relative presence they are there, or in absolute terms, how much of every element is present. All quantitative, semiquantitative and quantitative analysis can be carried out, and that is because of this mass spectrometer analyzer, which is highly sensitive and it is the quadrupole analyzer, which takes care of the mass-to-charge ratio. And, that is how it analyses. And, it is so versatile that the technique can substitute almost all traditional inorganic analytical techniques, such as ICP-AES, graphite furnace-AAS and flame-AAS, etcetera in analytical applicability. So, that means for these biological and pharma samples, the only answer for analytical tool is ICP-MS, because it can replace all others and it is definitely far more superior.

When I was showing you those graphs, I did show you the supremacy of ICP-MS. It was far beyond the graphite furnace or the ICP-AES and of course, certainly, with flame-AAS, which has no comparison between the other three. ICP-MS has been coupled to all forms of sample introduction or separation technique for spectral analyses, including the laser-assisted sample introduction, low pressure chromatography, high-pressure or high-performance liquid chromatography, gas chromatography, capillary electrophoresis and so on. So, it can be coupled with every such instrument, and therefore, all the separated components can be directly linked into the ICP-MS. As one of the most significant developments in analytical science nowadays, ICP-MS has been widely used in many industries. The application which was introduced into geological science research at first has rapidly enlarged to other fields including semiconductors, environmental, nuclear, chemical, clinical, research laboratories after 1984 when the first commercial instrument emerged. So, you see now, ICP-MS has a wide range of application. It can be used for semiconductors, for environmental samples, for nuclear science samples, for chemical science samples, clinical samples and research samples.

The principal and construction of ICP-MS – the principle construction of modern ICP instruments are basically identical on the whole. There is no main change; there is a ICP, which employs plasma, and that is why the name ICP for its ionization source, and there is a mass spectral analyzer. So, that is all that the machine has, but the standard of introducing the sample, the procedure for using different types of nebulizers – these vary in an ICP-MS machine when the sample changes from one to another.