A Beginner's Guide to ICP-MS

Part I

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Amazingly, 18 years after the commercialization of inductively coupled plasma mass spectrometry (ICP-MS), less than 4000 systems have been installed worldwide. If you compare this number with another rapid multielement technique, inductively coupled plasma optical emission spectrometry (ICP-OES), first commercialized in 1974, the difference is quite significant. In 1992, 18 years after ICP-OES was introduced, more than 9000 units had been sold, and if you compare it with the same time period that ICP-MS has been available, the difference is even more dramatic. From 1983 to the present day, more than 17,000 ICP-OES systems have been installed — more than four times the number of ICP-MS systems. If the comparison is made with all atomic spectroscopy instrumentation (ICP-MS, ICP-OES, graphite furnace atomic absorption [GFAA] and flame atomic absorption [FAA]), the annual turnover for ICP-MS is less than 7% of the total atomic spectroscopy market — 400 units compared to approximately 6000 atomic spectroscopy systems. It's even more surprising when you consider that ICP-MS offers so much more than the other techniques, including two of its most attractive features — the rapid multielement capabilities of ICP-OES, combined with the superb detection limits of GFAA.

ICP-MS — ROUTINE OR RESEARCH?

Clearly, one of the reasons is price — an ICP-MS system typically costs twice as much as an ICP-OES system and three times more than a GFAA system. But in a competitive world, the "street price" of an ICP-MS system is much closer to a top-of-the-line ICP-OES system fitted with sampling accessories or a GFAA system that has all the bells and whistles on it. So if ICP-MS is not significantly more expensive than ICP-OES and GFAA, why hasn't it been more widely accepted by the analytical community? I firmly believe that the major reason why ICP-MS has not gained the popularity of the other trace element techniques is that it is still considered a complicated research technique, requiring a very skilled person to operate it. Manufacturers of ICP-MS equipment are constantly striving to make the systems easier to operate, the software easier to use, and the hardware easier to maintain, but even after 18 years it is still not perceived as a mature, routine tool like flame AA or ICP-OES. This might be partially true because of the relative complexity of the instrumentation; however, in my opinion, the dominant reason for this misconception is that there has not been good literature available explaining the basic principles and benefits of ICP-MS in a way that is compelling and easy to understand for someone with very little knowledge of the technique. Some excellent textbooks (1, 2) and numerous journal papers (3–5) are available that describe the fundamentals, but they tend to be far too heavy for a novice reader. There is no question in my mind that the technique needs to be presented in a more user-friendly way to make routine analytical laboratories more comfortable with it. Unfortunately, the publishers of the "for Dummies" series of books have not yet found a mass (excuse the pun) market for writing one on ICP-MS. So until that time, we will be presenting a number of short tutorials on the technique, as a follow-up to the poster that was included in the February 2001 issue of *Spectroscopy*.

During the next few months, we will be discussing the following topics in greater depth:
- principles of ion formation
- sample introduction
- plasma torch/radio frequency generator
- interface region
- ion focusing
- mass separation
- ion detection
- sampling accessories
- applications.

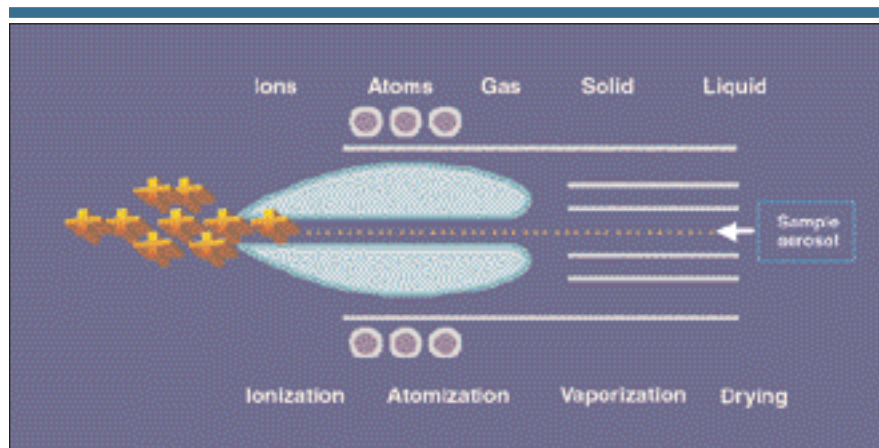We hope that by the end of this series, we will have demystified ICP-MS, made it

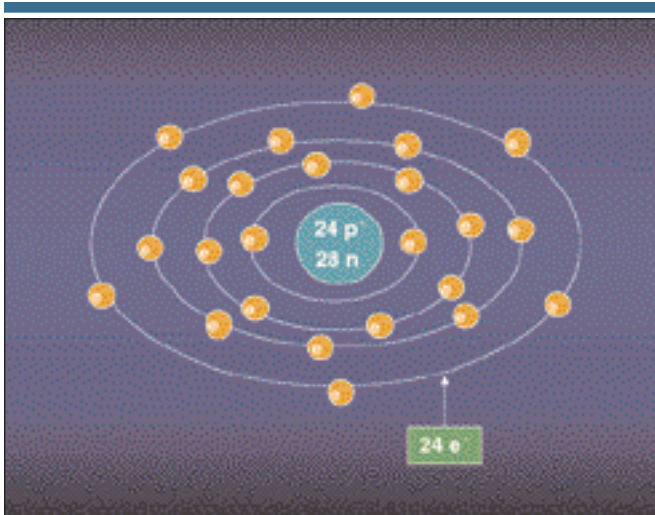**Figure 1.** Generation of positively charged ions in the plasma.

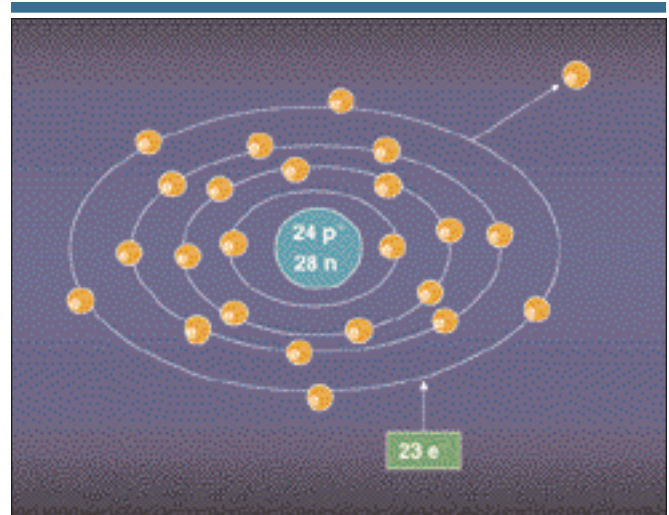**Figure 2.** Simplified schematic of a chromium ground-state atom (Cr⁰).

Figure 3. Conversion of a chromium ground-state atom (Cr⁰) to an ion (Cr⁺).

a little more compelling to purchase, and ultimately opened up its potential as a routine tool to the vast majority of the trace element community that has not yet realized the full benefits of its capabilities.

GENERATION OF IONS IN THE PLASMA
We'll start this series off with a brief description of the fundamental principle used in ICP-MS — the use of a high-temperature plasma discharge to generate positively charged ions. The sample, typically in liquid form, is pumped into the sample introduction system, which is made up of a spray chamber and nebulizer. It emerges as an aerosol and eventually finds its way — by way of a sample injector — into the base of the plasma. As it travels through the different heating zones of the plasma torch it is dried, vaporized, atomized, and ionized. During this time, the sample is transformed from a liquid aerosol to solid particles, then into a gas. When it finally arrives at the analytical zone of the plasma, at approximately 6000–7000 K, it exists as excited atoms and ions, representing the elemental composition of the sample.

The excitation of the outer electron of a ground-state atom, to produce wavelength-specific photons of light, is the fundamental basis of atomic emission. However, there is also enough energy in the plasma to remove an electron from its orbital to generate an ion. It is the generation, transportation, and detection of significant numbers of these positively charged ions that give ICP-MS its characteristic ultratrace detection capabilities. It is also important to mention that, although ICP-MS is predominantly used for the detection of positive ions, negative ions (such as halogens) are also produced in the plasma. However, because the extraction and transportation of negative ions is different from that of positive ions, most commercial instruments are not designed to measure them. The process of the generation of positively charged ions in the plasma is shown conceptually in greater detail in Figure 1.
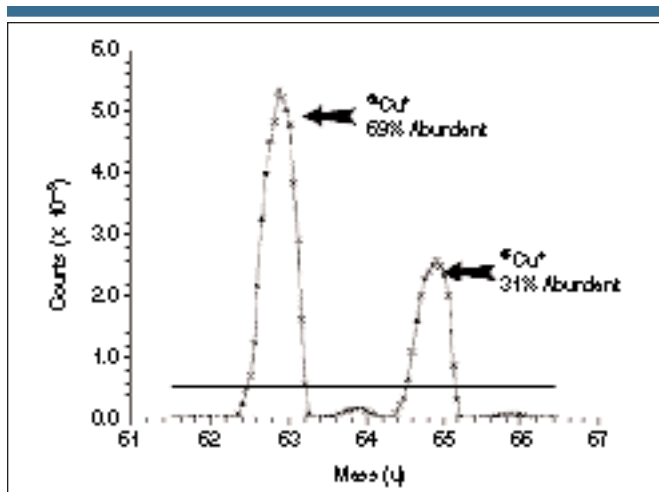
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Figure 4. Mass spectra of the two copper isotopes — $^{63}Cu^+$ and $^{65}Cu^+$.

Table I. Breakdown of the atomic structure of copper isotopes.

	^{63}Cu	^{65}Cu
Number of protons (p^+)	29	29
Number of electrons (e^-)	29	29
Number of neutrons (n)	34	36
Atomic mass ($p^+ + n$)	63	65
Atomic number (p^+)	29	29
Natural abundance	69.17%	30.83%
Nominal atomic weight	63.55*	

* Calculated using the formulae $0.6917n + 0.3083n + p^+$ (referenced to the atomic weight of carbon)

Figure 5. Relative abundance of the naturally occurring isotopes of all the elements (6). Reproduced with the permission of PerkinElmer Instruments (Norwalk, CT).

ION FORMATION

Figures 2 and 3 show the actual process of conversion of a neutral ground-state atom to a positively charged ion. Figure 2 shows a very simplistic view of the chromium atom Cr^0, consisting of a nucleus with 24 protons (p^+) and 28 neutrons (n), surrounded by 24 orbiting electrons (e^-) (It must be emphasized that this is not meant to be an accurate representation of the electrons' shells and subshells, but simply a conceptual explanation for the purpose of clarity). From this we can say that the atomic number of chromium is 24 (number of protons), and its atomic mass is 52 (number of protons + neutrons).

If energy is then applied to the chromium ground-state atom in the form of heat from a plasma discharge, one of the orbiting electrons will be stripped off the outer shell. This will result in only 23 electrons left orbiting the nucleus. Because the atom has lost a negative charge (e^-) but still has 24 protons (p^+) in the nucleus, it is converted into an ion with a net positive charge. It still has an atomic mass of 52 and an atomic number of 24, but is now a positively charged ion and not a neutral ground-state atom. This process is shown in Figure 3.

NATURAL ISOTOPES

This is a very basic look at the process, because most elements occur in more than one form (isotope). In fact, chromium has four naturally occurring isotopes, which means that the chromium atom exists in four different forms, all with the same atomic number of 24 (number of protons), but with different atomic masses (numbers of neutrons).

To make this a little easier to understand, let's take a closer look at an element like copper, which has only two different isotopes — one with an atomic mass of 63 (^{63}Cu) and the other with an atomic mass of 65 (^{65}Cu). They both have the same number of protons and electrons, but differ in the number of neutrons in the nucleus. The natural abundances of ^{63}Cu and ^{65}Cu are 69.1% and 30.9%, respectively, which gives copper a nominal atomic mass of 63.55 — the value you see for copper in atomic weight reference tables. Details of the atomic structure of the two copper isotopes are shown in Table I.

When a sample containing naturally occurring copper is introduced into the plasma, two different ions of copper, $^{63}Cu^+$ and $^{65}Cu^+$, are produced, which generate different mass spectra — one at mass 63 and another at mass 65. This can be seen in Figure 4, which is an actual ICP-MS spectral scan of a sample containing copper. It shows a peak for the $^{63}Cu^+$ ion on the left, which is 69.17% abundant, and a peak for $^{65}Cu^+$ at 30.83% abundance, on the right. You can also see small peaks for two Zn isotopes at mass 64 (^{64}Zn) and mass 66 (^{66}Zn) (Zn has a total of five isotopes at masses 64, 66, 67, 68, and 70). In fact, most elements have at least two or three isotopes and many elements, including zinc and lead, have four or more isotopes. Figure 5 is a chart that shows the relative abundance of the naturally occurring isotopes of all the elements.

During the next few months, we will systematically take you on a journey through the hardware of an ICP mass spectrometer, explaining how each major component works, and finishing the series with an overview of how the technique is being used to solve real-world application problems. Our goal is to present both the basic principles and benefits of the technique in a way that is clear, concise, and very easy to understand. We hope that by the end of the series, you and your managers will be in a better position to realize the enormous benefits that ICP-MS can bring to your laboratory.

REFERENCES

(1) A. Montasser, *Inductively Coupled Plasma Mass Spectrometry* (Wiley-VCH, Berlin, 1998).
(2) F. Adams, R. Gijbels, and R. Van Grieken, *Inorganic Mass Spectrometry* (John Wiley and Sons, New York, 1988.).
(3) R.S. Houk, V. A. Fassel, and H.J. Svec, *Dynamic Mass Spectrom.* **6**, 234 (1981).
(4) A.R. Date and A.L. Gray, *Analyst* **106**, 1255 (1981).
(5) D.J. Douglas and J.B. French, *Anal. Chem.* **53**, 37 (1982).
(6) *Isotopic Composition of the Elements: Pure Applied Chemistry* **63**(7), 991–1002 (1991).

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