Applications of ICP-MS in Homeland Security

Application

Homeland Security

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Abstract

Inductively coupled plasma mass spectrometry can be used as a powerful screening tool for the presence of toxic elements and chemicals in the environment. It has the ability to quickly and quantitatively screen many types of samples for toxic metals at ultratrace levels. When hyphenated with gas or liquid chromatography systems, it can also distinguish toxic from nontoxic species of most elements including radioactive forms. Using retention time locking and compound independent calibration, gas chromatography inductively coupled plasma mass spectrometry (GC-ICP-MS) has the potential to accurately identify and quantify a wide range of volatile toxic organic compounds without the necessity of possessing or analyzing standards for each target analyte. As such, when used in conjunction with other analytical techniques, inductively coupled plasma mass spectrometry can be a valuable tool in the arsenal against environmental terrorism.

Introduction

Toxicity can be either biological or chemical in nature. In the case of chemical toxicity, elemental analysis can play an important role in the rapid detection and identification of the key elements in environmental toxins. The toxicity of an element is dependent on a number of factors including the intrinsic toxicity of the element itself. Such toxic elements include arsenic, beryllium, cadmium, cesium, mercury, lead, tin, antimony, and uranium. The toxic mechanisms and degree of toxicity are different for each element and often different for different forms of the same element. For example, the toxicity of inorganic arsenic is highly dependent on the oxidation state, either As^{+3} or As^{+5} and also on the presence of an organic moiety such as a methyl group. Many forms of organic arsenic are not toxic at all. Other elements such as cobalt, chromium, copper, nickel, molybdenum, phosphorous, selenium, and zinc are essential trace nutrients. These elements are essential to good health at trace levels and in the proper form, but can be highly toxic at increased concentrations or in the wrong form. A good example is chromium which exists in two inorganic states. Cr^{+3} is an essential nutrient while Cr^{+6} is highly toxic and a known carcinogen. Another example is phosphorous which is essential to the manufacture of DNA and RNA, but as phosphine gas or organophosphorous pesticides

and warfare agents is among the most deadly of chemicals. In addition, some elements can exist as highly toxic radioactive isotopes which are toxic regardless of the chemical or oxidation state. The health risk of an element in the environment is also determined by the stability, bioavailability and environmental mobility of the particular species of the element. Furthermore, elements which pose no health risk individually can be combined to create extremely toxic organic molecules such as pesticides and chemical warfare agents (CWAs).

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) as an Elemental Analyzer

Clearly, simply detecting the presence of a particular element or elements in the environment is not always sufficient to determine the presence of risk. For elemental analysis to be really useful in rapid environmental risk assessment, it must possess a number of important characteristics including:

- Sensitivity - It must be able to easily detect the element at below the toxic threshold in the sample matrix.
- Selectivity - It must be able to distinguish between the toxic element(s)/isotope(s) and other sample constituents which may be much more abundant, but are not toxic.
- Universality - It must be able to detect all possible target elements in a single, rapid analysis.
- Ease of use - It must be simple enough for a technician to operate routinely.
- Robustness - It must be reliable, stable, and able to tolerate a wide variety of sample types.

ICP-MS possesses all these characteristics.

ICP-MS Principles of Operation

Simply put, the ICP-MS is a mass spectrometer (MS) whose ion source is a high-temperature inductively coupled argon plasma. The sample is introduced into the plasma as an aerosol, usually as a liquid sprayed through a simple nebulizer. In the plasma, the high temperature (6000–10,000 °K) atomizes and ionizes the sample creating positively charged atomic ions. (See Figure 1.)

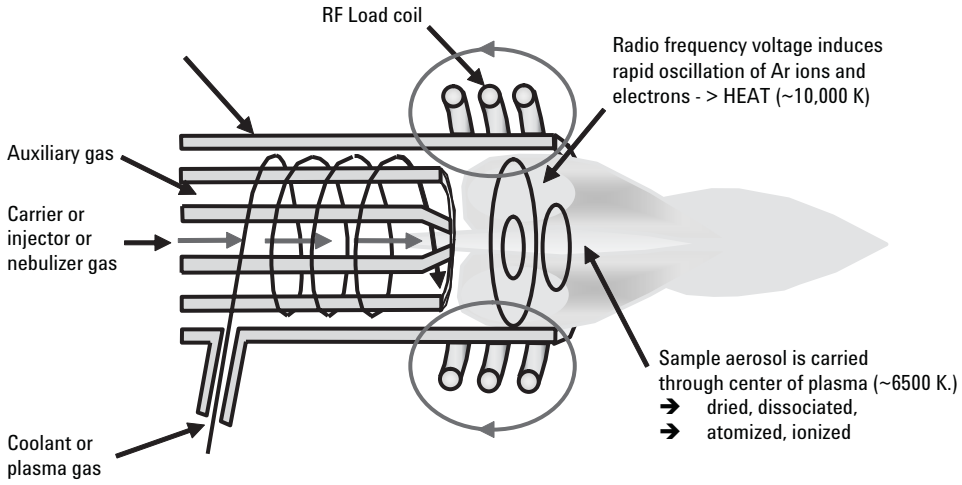

Figure 1. Diagram of ICP torch and plasma.

These ions are extracted into a vacuum region and focused into the MS via a system of orifices and electrostatic lenses. The MS, most often a quadrupole MS, sorts the ions by their mass to charge ratio and sends them to an electron multiplier (EM) detector for counting. (See Figure 2.)

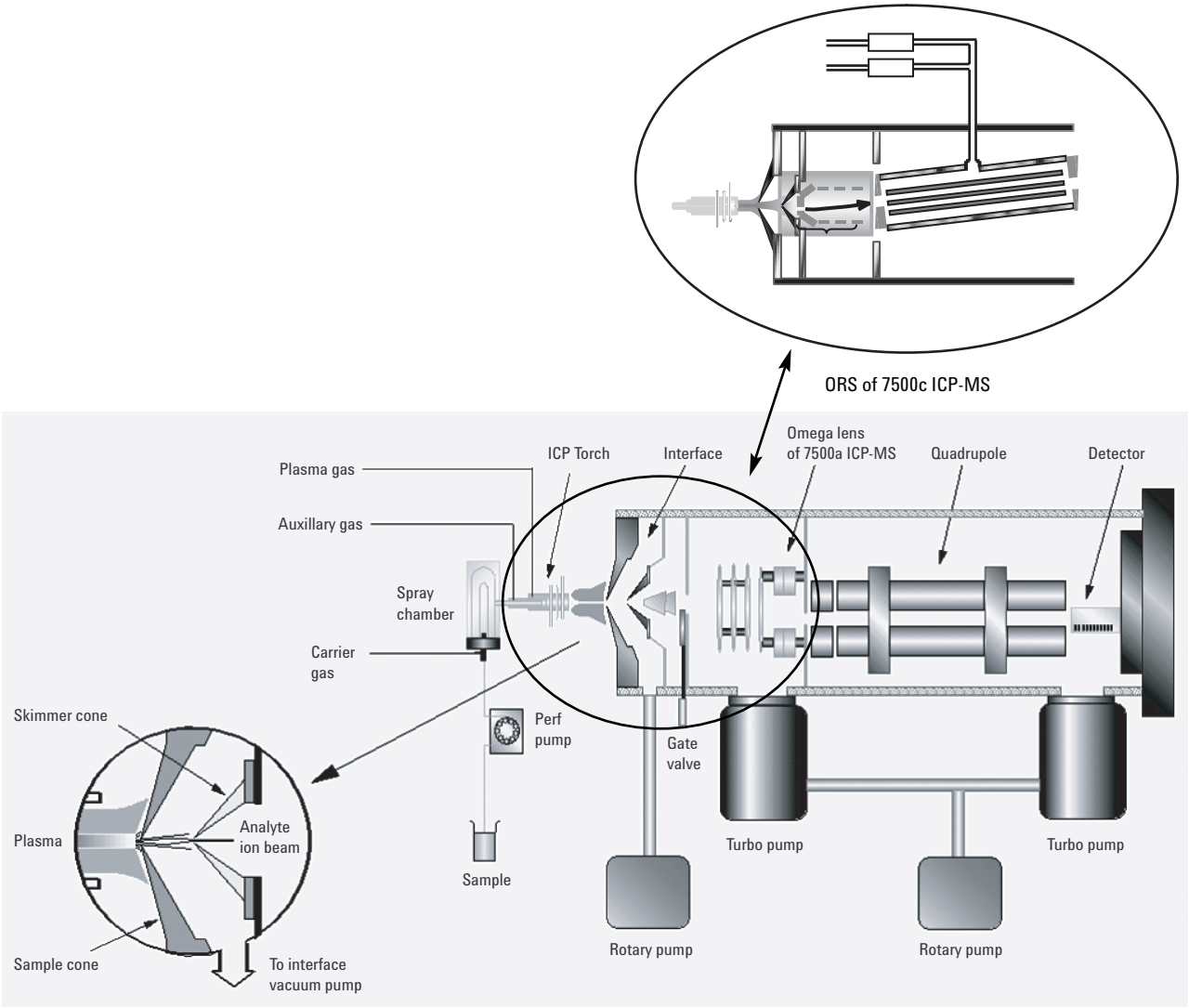

Figure 2. Diagram of Agilent 7500 Series ICP-MS instrument. Depending on the model, the Omega lens or Octopole Reaction System (ORS) may be present.

After processing, the output of the detector is a mass spectrum containing the mass and abundance of each ion (Figure 4). Each ion corresponds to an individual element or isotope in the original sample and the abundance is directly proportional to the original concentration. As a result, the ICP-MS spectrum is a simple accurate representation of the elemental composition of the sample. ICP-MS offers a number of advantages over other elemental analysis techniques. The most important are its extreme sensitivity, selectivity, and simultaneous multi-element capability. No other technique can deliver part-per-trillion (ppt) or sub-ppt detection limits (DLs) for almost the entire periodic table in a single scan taking just a few minutes. The only elements that are not directly measurable by ICP-MS are hydrogen, helium, neon, argon, and fluorine.

Simple Sample Preparation

For rapid screening of a sample for total elemental composition and concentration, the sample must be in a dissolved liquid form only, usually in dilute nitric or hydrochloric acid to maintain solubility with total dissolved solids less than about 0.5%. Most water samples can be analyzed without any additional preparation. Solid samples such as soils, sludges, plant materials, and foods must be digested in acid and diluted to the appropriate total dissolved solids and acid concentration. Since ICP-MS has the largest dynamic range of any elemental analysis technique (nine orders of linear dynamic range, Figure 3), sample preconcentration, dilution and reruns for out-of-range samples are not typically required.

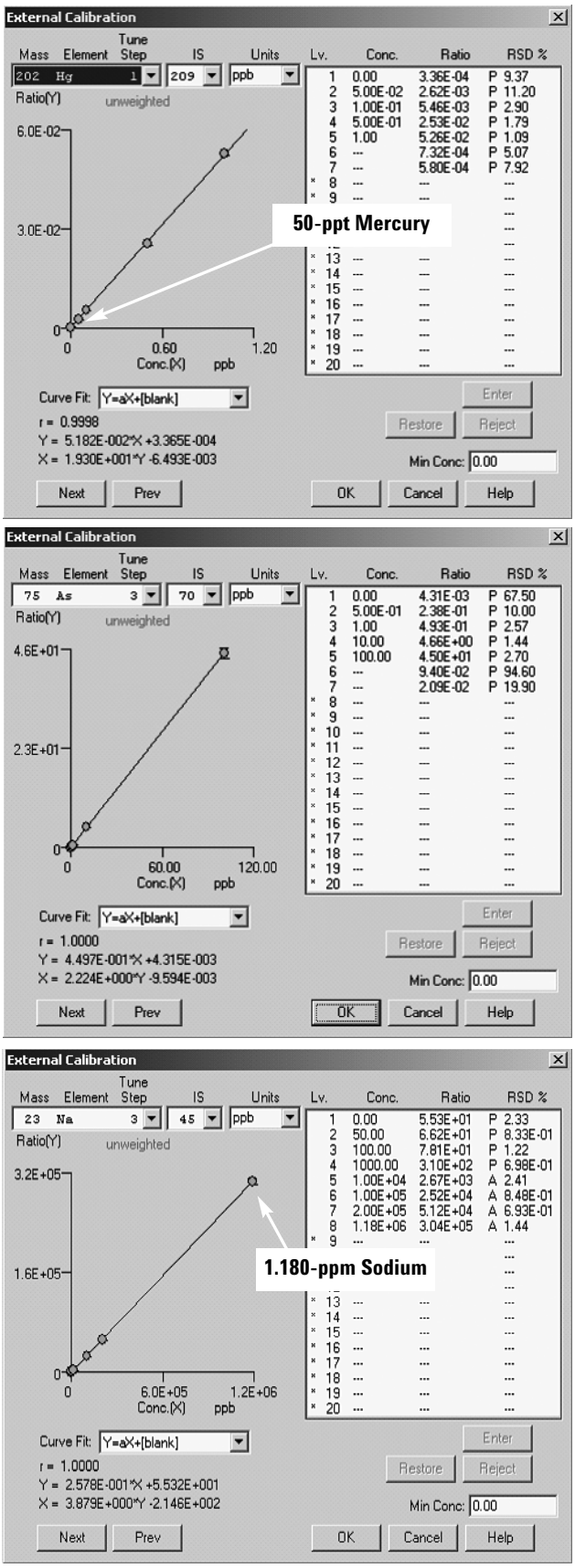

Figure 3. Calibrations for mercury, arsenic, and sodium at widely differing concentrations in a single sample analyzed under a single set of conditions.

Simple Data Analysis - Isotope Fingerprinting

The mass spectrum in Figure 4 was taken from a spiked extract of cinnamon. Each peak represents the mass and abundance of a particular isotope. Since most elements are made up of multiple isotopes that always occur at the same relative abundance in nature, both the presence of the individual isotopes and the ratio between the multiple isotopes can provide a "fingerprint" which positively identifies the element. The exploded section on the spectrum around mass 206 shows the four naturally occurring lead isotopes; 204, 206, 207, and 208. The bar graph is a template of the expected isotopic fingerprint overlaid over the measured isotope ratios by the software. The perfect match indicates that this is indeed lead and that the isotope ratios are normal. The presence of abnormal isotope ratios can be an indication of possible interferences or elements "artificially enriched" in one or more isotopes. This would be the case if the uranium spectrum showed elevated levels of the radioactive isotopes 234 and 235.

SemiQuant

Since ICP-MS reduces any sample to its simplest elemental constituents, that means that the response of any element is relatively independent of the matrix and the expected response of element can be calculated under a given set of conditions relative to the response of any other element. This is because the response of an element in ICP-MS is dependent on only the relative abundance of the particular isotope and the ionization potential of the element under the conditions measured. This leads to a powerful screening technique called "SemiQuant" in which both the composition and approximate (typically better than ±30%) concentration of a sample can be measured in a single analysis without any previous knowledge of the sample and without any external calibration. This is a powerful tool for rapidly screening large numbers of unknown and variable samples for the possible presence of toxic elements.

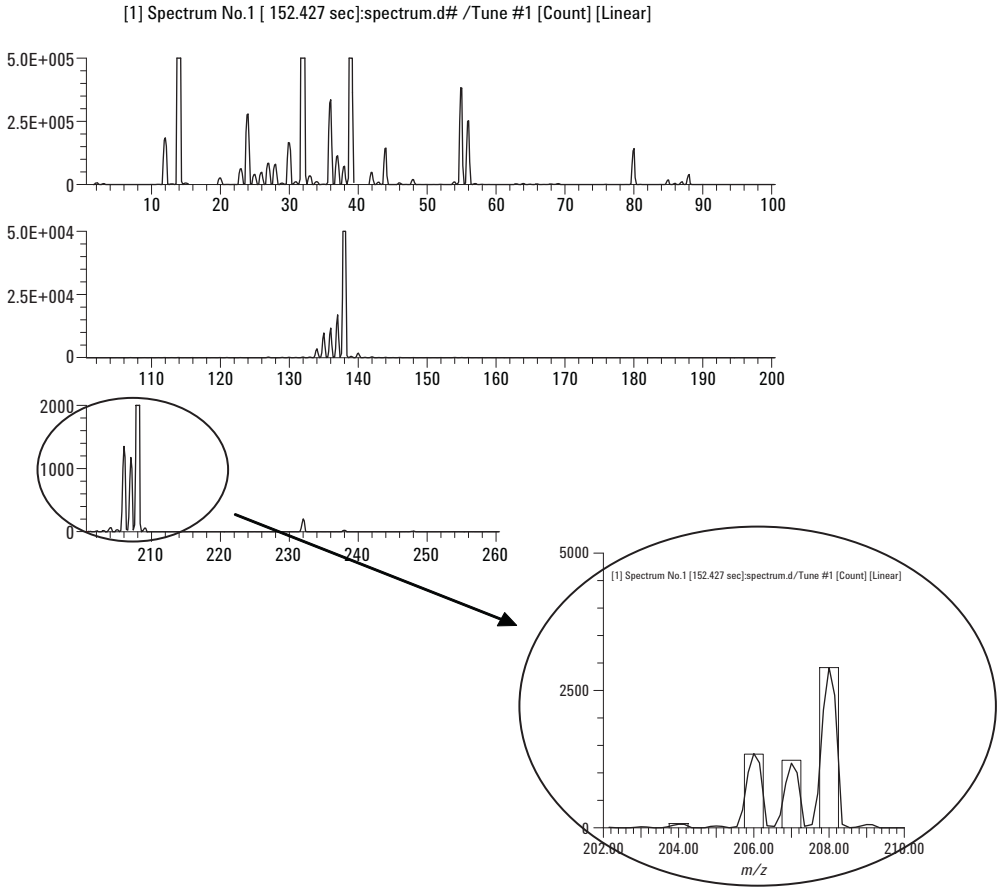

Figure 4. Full scan mass spectrum of spiked cinnamon extract showing relative abundances of elemental constituents. Enlargement shows isotope ratios of 10-ppb lead.

Elemental Speciation by Hyphenated ICP-MS

While total element analysis and semiquant are powerful tools, especially for initial screening of unknown samples, they cannot determine the elemental species or organometallic form of the element. Often, this information is necessary to determine the actual degree of risk, since the toxicity, bioavailability, and environmental mobility of an element can depend greatly on the form the element is present in. Additionally, information about the species of an element can help to trace the source of the contaminant in the environment. Hyphenated ICP-MS simply means connecting the ICP-MS instrument in series with another type of instrument to gain additional information about the sample. Typically the other instrument is some form of sample fractionation system such as a high performance liquid chromatograph (HPLC) or gas chromatograph (GC). In this case the ICP-MS becomes a very sensitive, selective elemental detector, very similar to liquid chromatography/mass spectrometry (LC/MS) or gas chromatography/mass spectrometry (GC/MS). However, there are significant differences, otherwise, there would be no advantage to using ICP-MS over the more conventional ionization techniques commonly used with LC/MS and GC/MS. In this case the differences are related to the superior sensitivity and elemental specificity of ICP-MS. ICP-MS can easily identify and quantify ppt levels of most elements eluted from an ion chromatograph. In this way, IC-ICP-MS (ion chromatography ICP-MS) can separate, identify, and quantify toxic ionic species in waters such as arsenic and chromium species. Using HPLC or GC coupled to ICP-MS, we can identify metal-containing organics of many types including toxic forms of arsenic, selenium, mercury, lead, tin, and others. The elemental specificity of ICP-MS makes it simple to locate all the compounds containing a target element such as phosphorous, sulfur, tin, mercury, etc. from the multitude of other compounds that show up by typical GC/MS or LC/MS. No other MS can offer this type of elemental specificity. An excellent example of this type of specificity is shown in Figure 5. This is a GC-ICP-MS chromatogram of a low sulfur reformulated gasoline [1]. The ICP-MS was set to look for carbon and sulfur and ignore everything else. The individual sulfur compounds in this gasoline sample are in the ppb range, while the individual carbon compounds are in the high ppm to percent range. Figure 5A shows the sulfur compounds by looking for sulfur 32, Figure 5B shows the carbon compounds in this case by looking at carbon 13. Carbon 13 was used for display purposes because it is only about 1% of the total carbon. The actual total carbon signal is 100 times higher. Here you can see the power of ICP-MS to find “the needle in the haystack”.

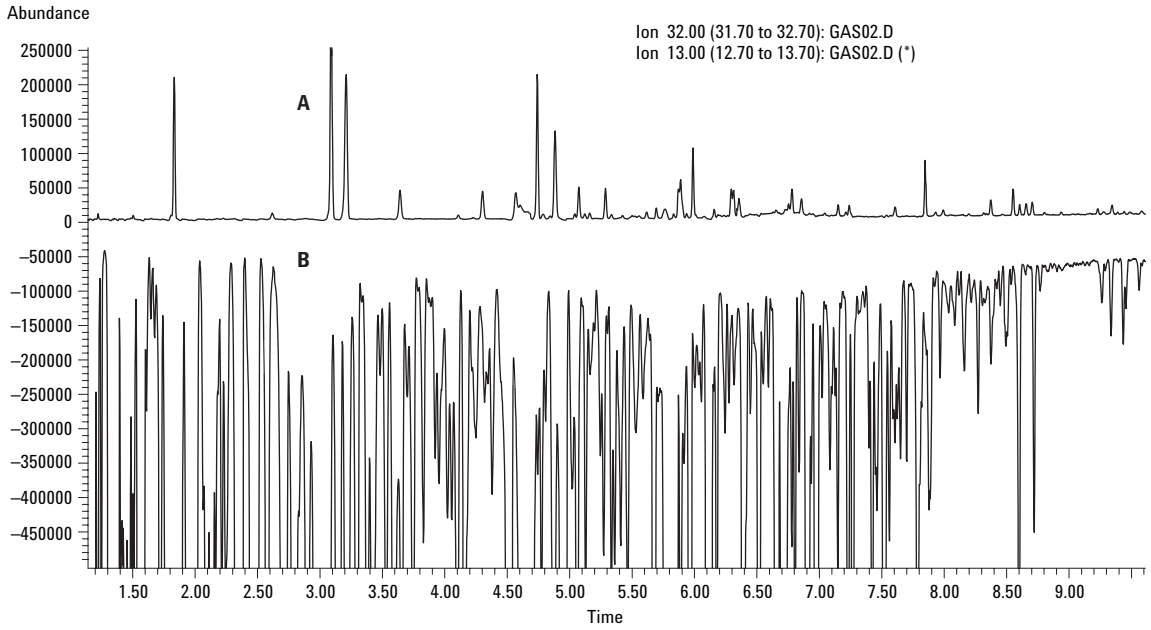

Figure 5. Chromatogram of low sulfur gasoline showing both the sulfer (A, upper chromatogram) and carbon (B, lower chromatogram) extracted element signals.

Screening for Pesticides and CWAs by LC and GC-ICP-MS

Figures 5, 6, and 7 show that ICP-MS can be used as a detector for both GC and LC for metals and nonmetals alike. It is especially powerful as a sulfur and phosphorous detector, though it can detect other metaloids, nonmetals and even halogens as well. Figure 6 shows a mixture of 15 pesticides analyzed by GC-ICP-MS [2]. The pesticides all contain either sulfur, phosphorous, chlorine, bromine, iodine, or a combination of more than one. The extracted element chromatograms show the extreme specificity of ICP-MS for each element.

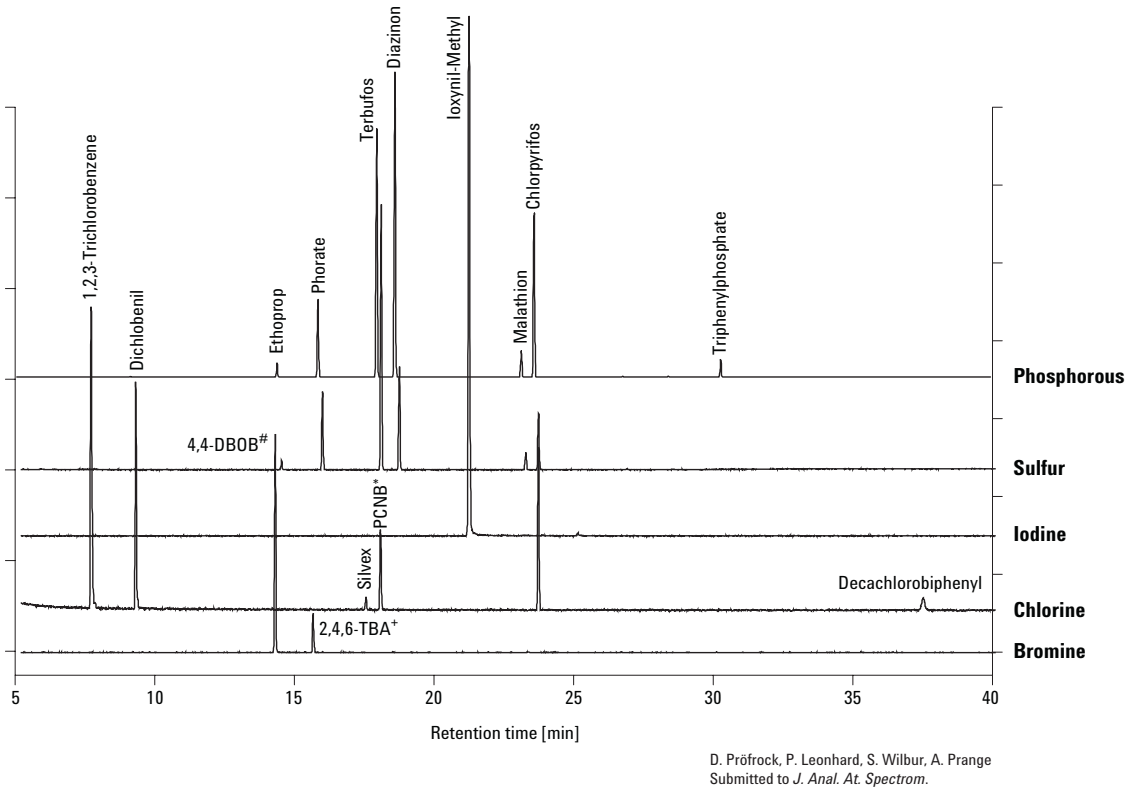

Figure 6. Extracted element chromatograms for a mixture of 15 pesticides containing sulfur, phosphorous, chlorine, bromine, and iodine.

Table 1 is a comparison of method DLs for several organophosphorous pesticides using GC with various phosphorous specific detectors as outlined in EPA methods compared to GC-ICP-MS detection limits for the same compounds [3]. GC-ICP-MS DLs for all four compounds are in the low ppt range, orders of magnitude better than the other techniques.

Table 1. Comparison of DLs for Selected Organophosphorous Pesticides by Conventional EPA Methods and GC-ICP-MS

Analyte	Instrument Limit of Detection (LOD) of U.S.EPA Method 507 (ppb)	Instrument LOD of U.S. EPA Method 526 (ppb)	Instrument LOD for ICP-MS calculated as per U.S. EPA (ppb)	LOD for ICP-MS calculated as per IUPAC (ppb)
Diazinon	26	30	0.2	0.012
Disulfoton	5.8	50	0.2	0.004
Terbufos	11	50	0.2	0.004
Fonofos	–	60	0.2	0.007

Figure 7 shows the results of the analysis of the polar phosphorous containing herbicides Glyphosate (Roundup), Gluphosinate and the metabolite aminomethyl phosphoric acid (AMPA), by ion pairing HPLC-ICP-MS [4]. DLs are in the 25–30 ppt per compound range compared with 10–50 ppb by other MS techniques [5].

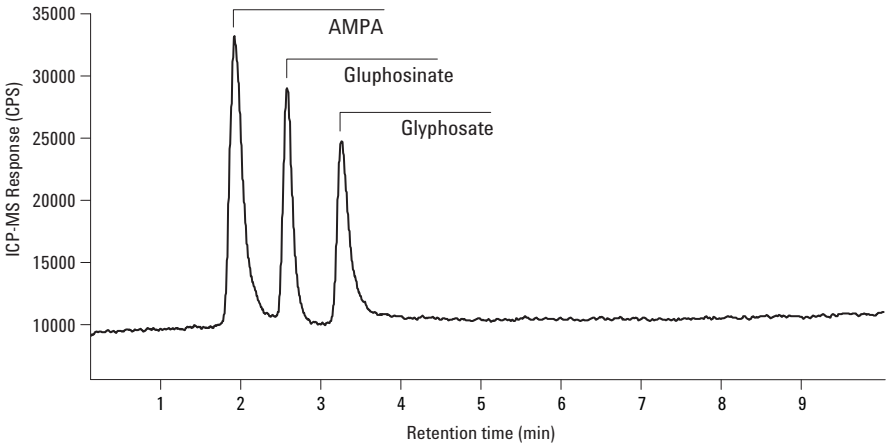

Figure 7. Chromatogram of 50-ppb mix of polar organophosphorous herbicides using ion-pairing HPLC-ICP-MS.

As a screening tool for toxic organics such as pesticides and CWAs, GC-ICP-MS offers some advantages over other specific detectors. One is its high sensitivity coupled with almost absolute specificity. DLs rival those of electron capture for heavier halogens including bromine and iodine without the lack of specificity of electron capture detector (ECD) and generally exceed those of GC/MS for most compounds under full scan conditions which are needed for screening. Second, since ICP-MS is an elemental detector, the response is element dependent, not compound dependent. This means that the response for a given element is the same regardless of the compound the element is present in. This allows the use of a technique called compound independent calibration. Compound independent calibration means that any compound whose identity is known can be quantified from the measured response of any of its constituent elements without compound specific calibration. Elemental response factors can be derived from a simple standard mix or internal standard containing the elements of interest. As a result, approximate quantification is possible for compounds for which there is no readily available standard, including dangerous chemicals such as CWAs. It is only necessary to know the identity of the compound which can be deduced from the relative retention time and partial elemental composition. The use of RTL (Retention Time Locked) compound libraries designed for GC/MS can greatly simplify this task.

Conclusions

As a rapid screening tool for the presence of toxic compounds of elements in the environment, ICP-MS offers several important advantages over other techniques.

- Rapid, semiquantitative ultratrace analysis of typical samples for most elements in a single scan
- Ability to distinguish radioactive isotopes and non-natural isotope ratios from naturally occuring isotopes
- When coupled to ion chromatography, allows determination of toxic versus nontoxic species of an element
- Highly sensitive, highly selective element specific detector for HPLC and GC for most elements
- Compound independent calibration in GC-ICP-MS allows quantitative measurement of unexpected compounds or compounds for which there is no standard available
- Does not require complex sample cleanup or preconcentration

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