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Trace and ultratrace analysis in liquids by atomic spectrometry

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Inductively coupled plasma mass spectrometry (ICP-MS) and ICP atomic emission spectrometry (ICP-AES) are widely used as routine techniques in analytical laboratories for multi-elemental determination at the trace and ultratrace level in liquid samples of quite different matrix composition. Limits of detection (LODs) varied between the ng/ml range in ICP-AES down to fg/ml range in ICP-MS for trace-element analysis in aqueous solution. Using special separation and enrichment techniques for analytes, the LOD can be improved (e.g., in ICP-MS, down to the sub-fg/ml range, which is relevant for special applications in microelectronics, and determination of long-lived radionuclides (e.g., Pu) in body fluids or in environmental samples). In addition, ICP-MS possesses the unique capability of measuring precise, accurate isotope ratios, which is applied in the precise determination of element concentrations by the isotope-dilution technique. In this article the capability, advantages and limits of ICP-MS and ICP-AES are examined as the most important multi-elemental atomic spectrometric techniques in comparison with atomic absorption spectrometry or atomic fluorescence spectrometry for the analysis of trace impurities in liquid samples.

Keywords: Atomic spectrometry; Inductively coupled plasma mass spectrometry; Inductively coupled plasma optical emission spectrometry; Metals; Radionuclides; Trace analysis; Ultratrace analysis

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1. Introduction

Atomic spectrometry [1–4] has become established with its ability to provide very sensitive, accurate, precise determinations of trace and ultratrace elements and species in liquid samples, such as high-purity solutions, environmental materials, different types of waters (rain, tap, river, sea or waste) [5], biological and medical fluids (blood, serum or urine) [6], or nuclear and radioactive waste solutions [7].

The most common aggregate state of samples investigated in atomic spectrometry is the liquid state. Besides the direct analysis of liquids with respect to impurities, aqueous solutions resulting from the digestion of solid samples (geological, biological and medical samples, metals, alloys or ceramics) and also organic solvents have often been investigated [8]. A range of spectrometric techniques is available, providing excellent tools for the trace and ultratrace analysis of liquids. This review concentrates on atomic spectrometric techniques, such as inductively coupled plasma mass spectrometry (ICP-MS), which has developed into one of the most important and powerful multi-element analytical techniques in comparison to the widely used ICP atomic emission spectrometry (ICP-AES) for the analysis of liquid samples with respect to determination of trace-element concentration. ICP-AES is used in many routine laboratories in the environmental area and in industry where a large number of elements have to be determined in many liquid samples (directly in solutions or in dissolved solids).

As a suitable ultratrace analytical technique, ICP-MS was developed by coupling an ICP source at ambient pressure with a quadrupole-based MS instruments by Gray and Date in 1975 [9]. At present, due to excellent limits of detection (LODs), ICP-MS is the most frequently used and very popular atomic spectrometric technique for a fast, sensitive multi-element determination at the trace and ultratrace concentration level for a wide variety of liquid samples [10]. This is demonstrated by the rapid growth of ICP-MS installations worldwide, such as different types of quadrupole-based Q or double-focusing sector field (SF) instruments (e.g., from Agilent, Perkin Elmer Sciex, Thermo Electron, Varian, and others).

About 20 years after the introduction of ICP-MS, there are more than 5000 ICP-MS instruments installed on the analytical market worldwide [11]. Instrumental developments (e.g., SF instruments with multiple-ion collection, introduced 12 years previously or the insertion of

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collision and reaction cells in order to reduce disturbing isobaric interferences), progress in ultratrace analytical methods, also in combination with on-line and off-line separation techniques (high-performance liquid chromatography (HPLC) and capillary electrophoresis (CE)), and routine capability, as well decreasing price and user-friendly maintenance, mean that sales are increasing by 10% every year [11].

The introduction of the reaction/collision cell in ICP-MS instruments (e.g., from Micromass, Perkin Elmer Sciex, Agilent or Thermo Electron) is one of the most significant improvements in ICP-MS instrumentation for more sensitive trace and ultratrace analysis and more precise determination of isotope ratios in comparison to commercial quadrupole ICP-MS without collision cell. The collision-induced reaction of ions, formed in the ICP, with molecules or atoms of the collision gas or gas mixture (e.g., He and/or H_2, O_2, Xe, CH_4 or NH_3) introduced into the collision or reaction cell results in a reduction of the energy spread (''cooling'') of the ions from several eV to <0.1 eV, and also in dissociation of the molecular ions and neutralization of disturbing atomic ions of the noble plasma gas (Ar contaminants) used. Tanner and co-workers reviewed collision-induced processes and reaction chemistry in a gas-filled collision or reaction cell for resolving interference problems in ICP-MS [12].

In addition to all other atomic spectrometric techniques, ICP-MS also allows a precise, accurate isotope analysis of chemical elements at low concentration range. This outstanding capability of ICP-MS is of interest in trace and ultratrace analysis for the application of isotope-dilution analysis (IDA), providing the possibility of absolute quantification for elements with two and more isotopes in any sample material, in order to obtain accurate trace-element concentrations. In IDA, one or two enriched isotope tracers of the element of interest (with well-known concentrations) are added to the sample. The determination of trace-element concentration is performed by measuring changed isotope ratios in the sample–spike mixture compared to those in the sample and highly enriched isotope tracer using the equation of IDA [13]. The precision (RSD, relative standard deviation) and the accuracy of the trace-element concentrations determined by ID-ICP-MS are in the low % range.

Simultaneously with the increase in the number of installations of ICP-MS worldwide, a rapid increase was also observed in the number of analytical publications (in J. Anal. Atom. Spectrom., Anal. Chem., Anal. Bioanal. Chem., Atom. Spectrom. or Spectrochim. Acta, Part B) in all fields of ICP-MS and of presentations (e.g., as demonstrated at the annual Winter Conference on Plasma Spectrochemistry and the annual Conference of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS) and others).

Atomic absorption spectrometry (AAS) is an important sensitive atomic spectrometric method that is suitable for the determination of selected elements at the trace and partly also at the ultratrace concentration level (e.g., using a graphite furnace for atomization of the sample (GF-AAS) and flame absorption spectrometry (FAAS)) in liquids. After enrichment of the analyte by ion-exchange SPE (solid phase extraction) in FAAS, LODs in the low and sub-μg/l are possible, as described for Cu, Zn and Fe determination in tap water by Kang et al. [14], whereas GF-AAS is, by comparison with FAAS, more sensitive and possesses lower LODs, which can be further improved by combination with enrichment procedures.

The general trend observed worldwide is that the well-established AAS for single or oligo-element analysis is being replaced by the effective ICP-AES and powerful ICP-MS in many laboratories to an increasing extent, if multi-element analysis is required, also as a result of the decreasing price of instrumentation, especially quadrupole-based ICP-MS, on the analytical market.

2. Principles of analytical techniques

In ICP-MS and ICP-AES, the liquid solution is nebulized using an effective pneumatic nebulizer [10], whereby the fine aerosol formed is transported with argon into the ICP torch. In the ICP (plasma temperature: 5000–8000 K), the chemical compounds (and the water matrix) are evaporated, the molecules are dissociated into their atomic constituents and the neutrals are excited and ionized. The main common parts of ICP-MS and ICP-AES are the solution-introduction systems and the ICP source and spectrometer, as shown in Fig. 1.

The ICP source was introduced into atomic spectrochemistry for the excitation (ICP-AES) or ionization (ICP-MS) of analytes, whereby the plasma is formed in a stream of argon gas flowing through the plasma torch consisting of three concentric quartz tubes. The energy is transferred to the argon gas at atmospheric pressure by means of a cooled induction coil made of copper using a radio-frequency generator. ICP-based instruments mostly operate with 27 or 40 MHz at an rf power of 1–2 kW. In AES, the energy of electrons and excited argon atoms (*via* collisions with analytes) in the ICP is used to convert the atoms and the molecules (formed after desolvation of aerosol and evaporation) into an excited state. If the excited electrons are returned to their ground state, the photons thus emitted are analyzed using an AES instrument. The atomic emission spectra obtained are very line-rich compared to ICP mass spectra.

In an ICP, positively single-charged and double-charged and also negatively charged ions and electrons are formed. For analytical purposes in ICP-MS, only positively charged ions are applied for MS analysis. The double-charged ions (e.g., $^{56}Fe^{2+}$ on $m/z = 28$ in the determination of $^{28}Si^{+}$) and molecular ions (e.g.,