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Analysis of high-purity solids by atomic emission spectroscopy and mass spectrometry with atom excitation and ionisation in inductively coupled plasma

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Abstract. Studies on procedures for the analysis of high-purity solids by inductively coupled plasma atomic emission spectroscopy and mass spectrometry published over the last decade are considered. The analytical scope of the methods is outlined. Specific features of sampling procedures, matrix effects and possibilities of decreasing the detection limits of impurities based on their preconcentration are discussed. The bibliography includes 95 references.

I. Introduction

The problem of substance purity control is always topical, because pure substances are used in the preparation of materials with special properties, which in turn determine parameters of devices constructed from these materials. At present, the influence of the trace element and its concentration, especially in the presence of other impurities, on the aim parameters of the device is often unknown. Therefore, the purpose of technological processes is to purify substances from all possible contaminants to the highest extent, which makes it necessary to monitor the purification process by analytical methods. These are characterised by the number of elements that can be detected and the detection limits of impurities (analytes). Up to the end of the previous century, spectrochemical techniques with arc excitation irradiation and mass spectrometry with spark or laser ionisation were widely used for the determination of the composition of impurities in high-purity substances. At present, these methods are virtually superseded by the methods of atom excitation and ionisation in inductively coupled plasma (ICP). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) and mass spectrometry (ICP-MS) are the most important of them. In these methods, atom excitation and ionisation are induced by an electrode-less discharge generated in an inductor high-frequency field in an argon atmosphere. As a rule, the capacity of generators employed in analytical instruments with ICP is up to 5 kW and the working frequency is 27.12 MHz. The capacity achieved in ICP is 1 – 2 kW. The electron temperature reaches 6000 – 8000 K, while the concentration of electrons is $10^{13} - 10^{16}$ cm^{-3}. Under such conditions, virtually total dissociation of molecules occurs, and atoms are effectively excited and ionised (the degree of ionisation of $> 75\%$ of the elements in the Periodic Table is $\sim 90\%$), and the portion of multiply ionised atoms is very low ($\sim 1\%$). This type of discharge has stable parameters, which ensures high (up to tenth parts of percent) reproducibility of the analytical signal. There are several ways to introduce samples into the ICP. Together with the traditional dispersion of solutions (either pneumatic or ultrasonic), vaporisation can be effected using an electrothermal atomiser (ETA) or by laser- or spark-induced dispersion (ablation). The low starting energy of ions (10 – 15 eV) and high stability of the plasma parameters enable the use of ICP ionisation in combination with relatively simple mass analysers of quadrupole or time-of-flight types.

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II. Instrumentation

The instruments for inductively coupled plasma atomic emission spectroscopy and mass spectrometry (ICP-AES and ICP-MS, respectively) are commercially available.

As regards the number of instruments for multielement analysis, those for ICP-AES produced by the instrument-making companies in the last decades play a leading role. Wide distribution of this equipment is due to low matrix effects, high reproducibility of the results, low detection limits for elements (down to 10^{-2} ng ml^{-1} or 10^{-7} mass % for solid samples) and relatively low cost (from USD 60 000 to 100 000). In the modern instruments for ICP-AES, linear detectors (as in spectrometers of the Pashen – Runge type) or matrix detectors (as in spectrometers with diffraction echelle gratings) with charge coupling and with charge carrier injection are used for recording the spectra. These detectors provide simultaneous photoelectric recording of the entire working range of wavelengths and allow complete automation of spectra processing using personal computers. The latest models of ICP spectrometers contain an option to perform axial measurement of plasma along with radial, which allows further reduction of the element detection limits (from two- to five-fold) due to an increase in the signal-to-noise ratio.[1, 2]

Recently, ICP-MS has acquired wide use due to excellent analytical characteristics, *viz.*, the possibility of simultaneous detection of up to 70 elements as contaminants in mineral acid solutions, including rare-earth elements (REE) and transuranium

elements, in a wide (up to 9 orders of magnitude) range of concentrations and with high (up to 99%) reproducibility. In the majority of publications devoted to mass spectrometric analysis of high-purity solids with the use of ICP, quadrupole mass spectrometers 'Plasma Quad' (Vacuum Generator, UK), 'ELAN' (Perkin Elmer, USA) and a magnetic sector fieldhigh resolution mass spectrometer 'ELEMENT' (Finnigan MAT, Germany) have been used most often. Note the higher cost of these instruments (from USD 80 000 to 300 000) as compared to those for ICP-AES.

An advantage of ICP-MS is the possibility of performing an isotope analysis.[3–5]

The resolution of a mass spectrometer is a crucial parameter determining the element detection limits. As a rule, the lowest detection limits (1–2 orders of magnitude lower than those achievable with quadrupole mass spectrometers) are provided by Finnigan MAT double-focusing instruments, due to the higher sensitivity, lower detector noise and the possibility of overcoming problems associated with overlap, in the analytical signal, of molecular ion lines and analyte lines generated in the ICP.[3,6,7]

One of the problems of using ICP-MS is the memory effect caused by deposition of a sample material on the introduction system and on parts of the separation and ion-beam formation devices. This effect can be reduced by high dilution of the sample solution (10^3-fold and larger), preliminary cleaning of the entrance cones (sampler and skimmer), prolonged (up to 2–3 h) washing of the sample introdution system with 2%–5% solutions of high-purity nitric or hydrochloric (sometimes sulfuric) acid.

The sample introduction system consists of a peristaltic pump, a nebuliser and a dispersion chamber. The peristaltic pump regulates the rate of solution feeding. The nebuliser and the dispersion chamber produce aerosol drops with sizes of 1–2 μm, which ensure equilibrium loading of the plasma and prevent its overcooling. Different constructions of dispersion chambers provide the uniformity of aerosol drop sizes or the sample particles in the case of laser ablation, thus reducing the element detection limits and random errors of the analysis.[8–10] With the use of pneumatic nebulisers, only ~1% of the analytical sample is transferred to the plasma, which decreases the efficiency of the sample usage. Ultrasonic nebulisers are about an order of magnitude more efficient.

III. Sampling procedures

Sampling procedures are determined, on the one hand, by the nature of the analysed material and, on the other hand, by the method of analysis and sample introduction into the ICP. One of the main steps in the analysis of high-purity solids by ICP-AES and ICP-MS is the dissolution of the sample. Dissolution eliminates the problems of non-uniformity of the sample, but instead brings a problem of importation of contaminants from the solvent. Those methods are preferred that require the least quantity of reagents. For example, dissolution in an autoclave was used for the analysis of indium,[11] and microwave-assisted dissolution for the analysis of pure carbon.[9] In certain cases, complete dissolution of analysed substances requires their preliminary fusion with alkali metal salts. For example, carbon ash samples were fused with lithium metaborate.[9] While choosing the solvent, it is necessary to keep in mind that this can damage the equipment parts. In particular, hydrofluoric, hydrochloric or sulfuric acid, even diluted to ~1% concentration, may cause corrosion of the metallic parts of the ion-beam forming system of the mass spectrometer.

For the ICP-AES, the admissible content of a matrix element in a solution is 1%–5%. In the case of ICP-MS, the concentration of a solid sample in a solution (preferably, in 1 M HNO_3) should not exceed 0.1%–0.05% to protect the instrument's entrance cones from the probe material deposition.[12] Such a dilution reduces the matrix effect. Due to the extremely low detection limits of analytes in solutions (up to several femtograms per ml) attainable with the double-focusing spectrometers, the detection limits of non-common contaminants in solids can reach 10^{-9} mass %–10^{-7} mass %.

When analysing high-purity substances using ICP-AES and ICP-MS, advantage is taken of introducing of sample into the ICP in the form of a vapour from an electrothermal atomiser.[13–16] The preliminary dissolution of the sample is still necessary for this method, however, the solution may not be highly diluted. Optimisation of the pyrolysis and evaporation temperatures and the use of matrix modifiers allows selection of the conditions for the separation of analytes from the matrix. In the determination of contaminants in high-purity phosphorus, arsenic, antimony, sulfur, tellurium and iodine, ICP-MS and ETA were used with preliminary thermal separation (80%–97%) of the sample matrix.[13] In simultaneous determination of 45 contaminants, detection limits of 10^{-7} mass % were reached, while in the case of optimised conditions for analysis for each element separately, they were as low as 10^{-8} mass %.

In a number of studies, the electrothermal analyser was fed with a homogeneous (for example, ultrasonicated) aqueous slurry of a finely dispersed sample rather than with its solution.[17–19] On the one hand, this method reduces the risk of contamination or analyte loss during the sampling, but on the other hand, it complicates the process due to the necessity of very fine desintegration of the sample (< 5–45 μm). Such a dispersity is achieved by treatment in special apparatuses for many hours. In the analysis of alumina, a dry sample mixed with a matrix modifier was introduced into the graphite atomiser.[20] In the determination of contaminants in coals by ICP-AES and ICP-MS, Ebdon *et al.*[21,22] introduced the samples directly into the ICP in the form of an aqueous suspension using the PTFE nebuliser for highly concentrated solutions.[23] Obviously, such a sampling procedure requires high dispersity of the sample and high uniformity and stability of the suspension. The sample content in the suspension was 0.2%–0.002% (ICP-MS) and 0.5% (ICP-AES). The same procedure was employed for the analysis of silicon nitride.[24]

At present, the search for new ways of introducing of powder samples into ICP without dissolution is in progress. For the direct introduction of powders into an instrument for ICP-AES, Bukar'[25] has used a special device. It is of note that certain difficulties are thus inevitable due to the low capacity of the ICP. The calibration problem becomes more serious due to the absence of standard samples adequate to the analytical ones. In our view, a more powerful (10–15 kW) plasma of double-jet arc plasmotron[26] is more promising for the direct analysis of powder samples.

The direct analysis of bulk solids by ICP-AES and ICP-MS is possible with the use of laser ablation (LA). The vaporisation of the material occurs under the action of a UV-laser (λ = 266 nm) focused on the sample surface to a spot 10–100 μm in diameter. With a plasma power density of 10^8–10^9 W cm^{-2}, non-selective sample vaporisation occurs. The aerosol is transported to the plasma by an argon flow. This method is especially efficient in the cases where solubilisation of the analytes without losses or contamination is complicated or for an express semi-quantitative analysis. The time- and labour-consuming steps of sample dissolution or desintegration are eliminated, and there is the possibility of local analysis. However, the non-uniformity of the sample and especially its surface can import essential errors into the results. LA-ICP-MS was used for the analysis of pure coal and graphite,[9,27] aluminium and copper[28] and a quartz glass.[29,30] Unfortunately, the detection limits in this method are usually not lower than 10^{-7} mass %–10^{-5} mass %.[27,31] Lower values (10^{-10} mass %–10^{-7} mass %) were reached only by Becker and Tenzler[29] in the analysis of a quartz glass with the use of a powerful IR-laser at a wavelength of 1064 nm. In this case, as opposed to the UV-laser case, the sample was decomposed by the plasma formed from the surrounding gas (argon), so it was unnecessary to focus the laser beam.[32]

Both laser and spark ablation are used in combination with the ICP-AES. By the examples of ICP atomic emission analysis of

a series of metals and alloys,[33] it was shown that the detection limits of analytes with the use of spark and laser ablation are comparable and have values of $10^{-6}\%-10^{-4}\%$. These limits depend on the matrix and the nature of the element under study. In this method, it is possible to spend substantially more sample material (as compared with the LA-ICP mass spectrometric method) without the risk of its deposition on the equipment parts.

It is possible to substantially reduce the detection limits of contaminants in solid high-purity substances by preconcentration. This refers in particular to the mass spectrometric method. For the preconcentration coefficient $K > 10^3$, *i.e.,* where the sample matrix is virtually completely separated, the detection limits, for non-common impurities can reach values comparable to those in pure water, *viz*., of about 10^{-11} mass $\%-10^{-10}$ - mass % (and even lower). It is substantial that preconcentration allows one to level the matrix effect, to avoid deposition of sample material on the entrance cones of the mass spectrometer, to eliminate the 'memory effect'[34] and to diminish the probability of overlap of lines of molecular ions of the matrix element and the analyte lines in the output signal. Numerous methods of preconcentration used in conjunction with ICP-AES and ICP-MS are sorption, chromatographic separation, extraction, distillation of the probe matrix (also in the form of a volatile compound) and its precipitation. A column for anion-exchange chromatography to separate the matrix (tantalum) from impurities was built directly into the system of sample introduction into the ICP.[10] Determination of contaminants in silicon and germanium on the ICP-MS spectrometer ELEMENT achieved their preconcentration by halogenation and distillation of the probe matrix from the solution.[35] The detection limits for the contaminants were 10^{-11} mass $\%-10^{-6}$ mass %. With the same mass spectrometer, the detection limits of fourteen rare-earth elements as impurities in lanthanum oxide of $10^{-10}\%-10^{-8}\%$ were reached following preliminary separation of the matrix from impurities by high-performance liquid chromatography.[36] The detection limits of the same order of magnitude were obtained with the use of the 'Plasma Quad3' mass spectrometer for fifteen contaminants in cadmium separated from the matrix by sorption.[37] Chromatographic separation of impurities from the matrix has been used [14, 15] in combination with ICP-AES and ETA for the analysis of lanthanum and cerium oxides.

The lowest possible detection limits of the common impurities could be achieved using minimum volumes of specially purified reagents, 'clean rooms', disposable glassware and special precautions to prevent contamination during sampling.[9, 10] The contaminants introduced during sampling were taken into account in a control experiment. It can be noted that the reagent-free methods of preconcentration are the most effective, since the extent of contamination in this case is a minimum. One of these methods is the vacuum distillation of the sample matrix. The preconcentration methods based on sample dissolution and its reaction with other reagents (in particular, with solid and liquid extractants) do not provide low detection limits for common impurities even at high preconcentration coefficient.[35]

IV. Matrix effects

Matrix effects related to ICP-AES and ICP-MS manifest themselves in the control of the aerosol droplet size and its transport to plasma, thermal properties of plasma, and spectral overlaps.[38] An efficient method of compensating non-spectral matrix effects is the use of an internal standard.[39] Usually, the role of the internal standard introduced into the sample solution is played by a chemical element not to be determined and is absent from the sample and from the control experiment (most often, indium, rhodium and single-isotope rare-earth elements are used). In the LA-ICP-MS, the working gas components (krypton, xenon) and molecular ions of the matrix (MAr^+, MO^+ where M is the matrix element) serve as the standards. In the analysis of a quartz glass by this method, the compensation of the signal instability by virtue of the internal standard $SiAr^+$ allowed one to decrease four- to five-fold the random error.[30]

Spectral overlaps of the analyte lines, mainly with the molecular ions, are among the main limitations of the mass spectrometric method. Steep gradients of the plasma density and temperature in the plasma beam formation area favour the formation of different molecular ions, the mass spectra of which override the spectra of the analytes. In particular, components of the solvent (H_2O, HNO_3, H_2SO_4, $HClO_4$, HCl) can serve as one of the sources of molecular ions,[9, 40] which combine with the sample matrix element and with argon to form MCl^+, MO^+, MN^+, $^{40}Ar^{35}Cl^+$, $^{40}Ar^{16}O^+$, $^{40}Ar^{14}N^+$, and also argides (MAr^+), oxides (MO^+), hydrides (MH^+) and other compounds of the matrix elements with the plasma components. Elements from the matrix modifiers also participate in molecular ion formation.[18] The sample introduction into the ICP by laser ablation allows elimination of these interference sources (except for MAr^+). The problem of molecular ion line overlap is especially vital for the light elements with atomic masses <80 a.m.u. Possible overlaps of the molecular ion lines and atomic ones from $^{24}Mg^+$ to $^{76}Ge^+$ are documented.[41] The paper cited also contains a discussion of the problems of element determination in different matrices using a double-focusing mass spectrometer with a resolution up to 10 000.

Systematic studies of molecular ion formation have been carried out.[42–45] The problem of molecular ion overlap in the mass spectrometric analysis of dissolved coal samples with the use of ICP and LA was considered in detail.[9] Possible approaches to avoid these overlaps are also discussed. It is obvious that the ability to solve the problem of overlaps depends on the resolution of the instrument. They can largely be avoided by the use of double-focusing mass spectrometers with medium (3000–4000) and high (10000) resolution. However, the use of high resolution in these instruments leads to an increase in the element detection limits due to the reduced ion transfer efficiency.[3] The intensity of molecular ion lines can be reduced by their 'desolvation' in special collision cells. Molecular ions decompose in these cells due to collisions with the filler gas. For example, a collision cell was used [46] in the analysis of pure graphite by LA-ICP-MS on a quadrupole mass spectrometer. By the example of the reduction of intensity of $^{40}Ar^{16}O^+$ and $^{40}Ar^{14}N^+$ lines, which complicate the determination of iron in graphite, the efficiency of a collision cell with hydrogen and helium as filler gases is shown. The fundamental aspects and the practical usage of collision cells in mass spectrometric analysis have been considered.[47] It should be noted that the so-called isobaric interferences, *i.e*., overlap of the lines of the matrix element oxides and those of the analyte isotopes with equal masses still present an unsolved problem. This problem is especially critical in the case of the determination of REE contaminants in rare-earth-containing matrix materials, for example,[159] of Tb in neodymium oxide ($^{143}Nd^{16}O^+$).

Usually, in the ICP-AES method it is possible to find analytical lines free from overlap. Otherwise, chemometric methods and the subtraction of control spectra from the sample spectra are used to account for the overlap.[48] Fractional evaporation of impurities and the matrix in the form of fluorides from a graphite atomiser was used in the analysis of alumina by ICP-AES in order to suppress the non-spectral matrix effects.[48]

V. Quantitative analysis

The advantages of the use of ICP as a tool for excitation and ionisation of atoms in the analysis of solutions of high-purity solids include the possibility of using aqueous solutions of analytes as standards and the ease of using the methods of additives and isotopic dilution. For example, the method of additives in atomic emission spectroscopy was successfully used for the determination of impurities in alumina, gallium and scandium oxides.[20, 49, 50] The influence of the matrix on the analytical signal value is levelled owing to the use of an internal

standard.[8,9,51–56] Reliable results were obtained in the mass spectrometric analysis with use of the isotopic dilution method and introduction of a suspension into the ICP [19] and the method of additives with aqueous solutions of the analytes.[18,20,31]

It is much more difficult to obtain quantitative results from the LA-ICP-MS due to the absence (as a rule) of certified standards. Some researchers employ calibration by analyte solutions for determination of the relative sensitivity coefficients using the standards with the similar matrix.[27] With internal standards, the correction of different sensitivity of mass spectrometric methods based on ICP only or LA-ICP is also possible.[31,57] Specially synthesised standards based on the material to be analysed are also employed. For example, such samples were used [58] in the LA-ICP mass spectrometric analysis of GaAs. Becker [46] proposed an original method of calibration by LA-ICP-MS in the analysis of graphite: an aqueous solution of the analyte passed through the nebuliser is mixed with high-purity graphite atomised by laser ablation, and the graphite sample atomised in the same way is mixed with the pure solvent. In the author's opinion, this method allows one to obtain reliable results and to reduce the detection limits for a series of elements due to the reduction of the background level and the increase in the sensitivity coefficient.

For the verification of the correctness of the result of analysis, the method 'added–found' is often used,[59–61] together with comparison with the results from independent analytical methods [18,20,62] and with those obtained for synthetic standards. The most reliable results are obtained where the certified standards are used. Unfortunately, their list for the high-purity substances is short. Standards of the SARM, BCR and NIST series (SRM 1635, SRM 1630a, SRM 1632b and SRM 1633b) are used for the ICP-MS analysis of coal and ash,[9,17,19] NIST (SRM 8171) for the analysis of silver,[63] NIST (SRM 681) for platinum,[31,46] NIST (SRM 699) for alimina,[18,20] State Standard Sample 7287-96 for gold,[64] JCRM (R004) and JCRM (R005) for Si_3N_4,[24] CRM (JSS 003-2) for iron,[65] and silicate glasses NIST (SRM 610-615) for the analysis of oxide crystals.[66–68] According to the results of the inter-laboratory measurements, these glasses contain ~50 elements as impurities in the 1×10^{-4} mass % – 5×10^{-2} mass % concentration range.

As a rule, in all versions of ICP-AES and ICP-MS, the random error of element determination is not larger than 10%, and sometimes it is much lower.

VI. Specific analytical procedures

Properties of materials used in semiconductor and nuclear engineering, as well as in micro- and optoelectronics, are extremely sensitive to the content of impurities. Therefore, analytical monitoring in all steps of the purification technology of these materials is very important. At present, the methods discussed above are the leaders in the field of such monitoring.

It is of note that numerous procedures are devoted to the determination of contaminants in REE oxides, the majority of them being developed and published in China. The problems of atomic-emission spectroscopic analysis of REE are related to the multilinear character of their emission spectra. A general approach to the development of procedures for the quantitative determination of contaminants in pure REE and their oxides was proposed,[60] which is based on the preliminary quantitative determination of the matrix effect on the analytical signal.

The main data on the specific analytical procedures for pure substances using atomic emission spectroscopy and mass spectrometry are summarised in Tables 1 and 2.

Table 1. Methods of analysis of some pure metals, semiconductors and other substances by ICP-AES and ICP-MS.

Matrix	Method	Instrument		Sampling procedure	Contaminants determined	C_{min}	Ref.
		name	manufacturer				
Cadmium, zinc, copper, gallium	MS	ELEMENT	Finnigan MAT	dissolution in HNO_3 + HCl, 2 g litre^{-1}	34 elements	10–16 ng litre^{-1}, $(5-8)\times10^{-7}$ mass %	12
Cadmium	MS	Plasma Quad 3	VG Elemental	dissolution in HNO_3 + HCl, sorption of impurities on Dowex 50W-X 8, dissolution of sorbed impurities in HNO_3	Ti, V, Cr, Ni, Mn, Co, Cu, Zn, Sr, Cs, Ba, La, Gd, Lu, Pb	$(0.3-5)\times10^{-8}$ mass %	37
	MS	–	–	ion-exchange preconcentration	Cu, Zn, Pb, Fe	–	69
Tellurium	MS	POEMS	Thermo Jarrell Ash	dissolution in HNO_3, co-precipitation of impurities with $Fe(OH)_3$, dissolution of the precipitate in HNO_3, dilution with water	Bi, Sn, Pb, In, Tl, Cd, Cu, Co, Ni, Zn, Ti, Be, Zr	$n\times10^{-5}$ mass % and lower, except for Pb and Zn	34
Phosphorus, sulfur, arsenic, selenium, antimony, tellurium, iodine	MS	Plasma Quad 2+, ETV Mk II	VG Elemental	dissolution in H_2O_2 (portion of 1 g, 10% solution of the sample), evaporation from a graphite atomiser. Thermal separation of the matrix from impurities	57 elements	$n\times10^{-7}$ mass % – $n\times10^{-6}$ mass %	13
Silicon, germanium	MS	ELEMENT	Finnigan MAT	dissolution of a sample (1 g) in a closed beaker in a mixture of acids ($HF+HNO_3$ for silicon and $HCl+HNO_3$ for germanium) at 70–75 °C, concentration of a solution to ~50 μl, dissolution of the precipitate in 1 M HNO_3 (5 ml)	64 elements	$n\times10^{-11}$ mass % – $n\times10^{-6}$ mass %	35

Table 1 (continued).

Matrix	Method	Instrument		Sampling procedure	Contaminants determined	C_{min}	Ref.
		name	manufacturer				
Quartz glass	MS	Elan 6000 laser Nd : YAG, $\lambda = 1064$ nm, $W = 10^9 - 10^{10}$ W cm^{-2}	Perkin Elmer	laser ablation	Li, B, Na, Mg, Al, K, Ca, Ti, V, Cr, Fe, Mn, Cu, Zr, Ba, Pb	$n \times 10^{-7}$ mass % – $n \times 10^{-5}$ mass %	29
	MS	HP 4500 laser Nd : YAG, $\lambda = 1064$ nm, $W = 10^9 - 10^{10}$ W cm^{-2}	Agilent Technologies	the same	Na, Al, Ca, Ti, Cr, Mn, Zr, Ba, Pb	$n \times 10^{-6}$ mass % – $n \times 10^{-5}$ mass %	30
Quartz	AES	JY 2000	Jobin Yvon	simultaneous dissolution in an autoclave of 17 samples (1 g portions) in HF vapour, distillation of the sample matrix in the form of SiF_4, dissolution of the precipitate in 2% HNO_3	Na, K, Ca, Fe, Ti	$n \times 10^{-6}$ mass %	70
	MS	VG Plasma Quad PQ 3	VG Element	the same	Li, Mg, Al, V, Cr, Mn, Co, Ni, Cu, Zn, Mo, Cd	$n \times 10^{-8}$ mass % – $n \times 10^{-7}$ mass %	70
Silicon nitride	AES	Monochromator JY138	Jobin Yvon	dissolution in an autoclave in a mixture of HF, H_2SO_4 and HNO_3 or preparation of 1% suspension	Ca, W, Co, Al, Fe, Mg, Na	–	24
Gallium	MS	Plasma Quad 3	VG Elemental	partial dissolution of 2 g of gallium in $HCl + HNO_3$ (more noble impurities are concentrated in the insoluble residue). The dissolved impurities (Al, Cd, Mn), are concentrated by extraction with isobutyl methyl ketone	Ag, Bi, Co, Cu, Fe, Ni, Pb, Al, Cd	$n \times 10^{-7}$ mass % – $n \times 10^{-8}$ mass%	71
	MS	–	–	extraction of the sample matrix with diisopropyl ether	–	0.006 – 0.082 mg litre^{-1}	39
	AES	JY-2000	Jobin Yvon	dissolution in HNO_3, treatment with HF for the separation of the matrix by precipitation of GaF_3. Electrothermal atomisation	Au, Ba, Bi, Cd, Co, Cr, Cu, Mg, Mn, Pb, Pd, Pt, Rh, Tl, Zn	10^{-7} mass % – 10^{-6} mass%	49
Arsenic	MS	Plasma Quad 3	VG Elemental	dissolution of a 250 mg sample in aqua regia vapour. Separation of the sample matrix by distillation of bromide from a solution in $H_2SO_4 + HBr$ or by sorption on Dowex 50W-X 8	Mg, Al, V, Cr, Mn, Fe, Ni, Co, Zn, Cu, Ga, Sr, Zr, Mo, Cd, In, Ba, Cs, Tl, Pb, Bi, La, Ce, Gd, Lu	$n \times 10^{-8}$ mass % – $n \times 10^{-7}$ mass %	40
Gallium arsenide	MS	ELEMENT	Finnigan-MAT	chlorination of GaAs by gaseous Cl_2 at 280 °C with simultaneous distillation of gallium and arsenic as chlorides, dissolution of the residue in 1 M HNO_3	B, Mg, Al, Si, Ca, V, Cr, Mn, Fe, Ni, Zn, Sn	3×10^{-8} at.% – 1×10^{-6} at.%	58
				laser ablation	Tc, I, Th, U	$< 1 \times 10^{-7}$ mass %	58
Indium	AES	ICAP 61	Thermo Jarrell Ash	dissolution in an autoclave in HCl, 1% indium solution	21 elements	$n \times 10^{-5}$ mass % – $n \times 10^{-3}$ mass %	11
				precipitation of indium in the form of oxychloride		lowering by 5 – 100 times	
	MS	Plasma Quad	VG Elemental	dissolution in an autoclave in HCl, 0.1% indium solution	40 elements	$n \times 10^{-6}$ mass % – $n \times 10^{-3}$ mass %	11
Graphite	AES	Nippon, model ICAP-55	Thermo Jarrell Ash	decomposition of 0.5 g of graphite in a mixture of $HNO_3 + H_2SO_4$ in a microwave oven	Li, Na, K, Mg, Ca, Sr, Al, Fe, Ni, Cr, Ti, V	$n \times 10^{-5}$ mass % – $n \times 10^{-4}$ mass % (under the optimum conditions for each element)	72

Table 1 (continued).

Matrix	Method	Instrument		Sampling procedure	Contaminants determined	C_{min}	Ref.
		name	manufacturer				
Graphite	AES	ICPS 2000	Shimadzu	decomposition of a 0.5 g portion in a mixture of H_2SO_4, $HClO_4$ and HNO_3 (5 : 3 : 1) at 200 °C, removal of the excess $HClO_4$ and HNO_3 at 150 °C, dilution with water to 100 ml	Ca, Fe, Ni, Sr, Ti, V	$n \times 10^{-5}$ mass % – $n \times 10^{-4}$ mass %	73
	MS	Elan 6000, CETAC LSX-200	Perkin Elmer, Cetac Technologies	laser ablation	Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Y, Lu, U	$n \times 10^{-7}$ mass % – $n \times 10^{-6}$ mass %	27
Coal	MS	HR-ICP-MS	Finnigan MAT	fusion with lithium metaborate, dissolution in a mixture of H_2O_2, HNO_3 and HF in a microwave oven	70 elements	$n \times 10^{-8}$ mass % – $n \times 10^{-4}$ mass %	9
	MS	UV Laser Probe	Finnigan MAT	blending with a coal powder, containing an internal standard (In), pressing into pellets		$n \times 10^{-7}$ mass % – $n \times 10^{-4}$ mass %	
	AES	ARL 3580	ARL	fusion with lithium metaborate, dissolution in a mixture of H_2O_2, HNO_3 and HF in a microwave oven	–	–	9
	MS	ELAN 6000	Perkin Elmer	suspension (1.3 mg ml^{-1}) in 5% nitric acid	As Mn	0.06 pg 0.06 pg	17
	MS	HGA 600 MS	Perkin Elmer	electrothermal atomisation in the presence of NaCl (physical carrier) and matrix modifier (Pd)	Pb Se	0.12 pg 0.36 pg	17
Coal, coal ash	MS	ELAN 6000, HGA 600 MS	Perkin Elmer	uniform suspension, electrothermal atomisation in the presence of matrix modifiers. Isotopic dilution	Cd Hg Tl Pb	6×10^{-6} mass %, 1.4×10^{-5} mass %, 1×10^{-6} mass %, 1.2×10^{-4} mass %	19
Aluminium	MS	–	–	separation of a matrix from impurities by sorption	Fe, Ni, Co, Cu, Zn, Ag, Cd, Ga, In	$n \times 10^{-9}$ mass % – $n \times 10^{-7}$ mass %	74
	AES	Philips PV 8210	Philips	dissolution in HCl (1 : 1) in the presence of a catalyst (Pd) with addition of HNO_3 at 45 – 55 °C,	21 elements	10^{-6} mass % – 10^{-4} mass %	75
				extraction of analytes with bis(2-ethylhexyl) dithiophosphate and bis(2-ethylhexyl)phosphate after dissolution of a 1 g sample at 45 – 55 °C in HCl (1 : 1) in the presence of a catalyst (Pd) with addition of HNO_3	Ti, Ga, Ni, Se, Te, Cd, Co, Bi, Pb, Cu	$n \times 10^{-7}$ mass % – $n \times 10^{-6}$ mass %	75
	AES	IRIS Advantage, SSEA	Thermo Jarrell Ash	spark ablation	26 elements	$n \times 10^{-6}$ mass % – $n \times 10^{-4}$ mass %	76
Aluminium oxide	MS	ELAN 5000, HGA 600	Perkin Elmer	preparation of a uniform suspension, electrothermal atomisation in the presence of a matrix modifier ($PdCl_2$)	Na, Mg, Ca, V, Mn, Fe, Ni, Ga	$n \times 10^{-6}$ mass % – $n \times 10^{-3}$ mass %	18
	AES	Spectroflame, ETY 4000	Spectro, Spectral System	blending of a sample with a matrix modifier (AgCl) in a 1 : 1 ratio, electrothermal atomisation	Fe, Ga, Mg, Mn, V, Zn	$n \times 10^{-6}$ mass % – $n \times 10^{-4}$ mass %	20
	AES	Monochromator WDG 500-1A,	Beijing Second Optics	1% emulsion of Al_2O_3 in an aqueous solution of Triton X-100, HNO_3 and PTFE	Cr, Cu, Fe, V	$n \times 10^{-6}$ mass % – $n \times 10^{-5}$ mass %	48
		ICP HGA 500	BBE Factory [a]	fluorination of the matrix and impurities in a graphite atomiser			
Niobium oxide, tantalum oxide	AES	ICAP 61	Thermo Jarrell Ash	autoclave decomposition (4 atm) in a microwave oven in a mixture of HF and HNO_3 (6 : 1), addition of H_2SO_4, concentration, dissolution of the residue in 1% – 4% ammonium oxalate. Sorption preconcentration on Polyorgs VII	22 elements	without preconcentration $n \times 10^{-4}$%	77

Table 1 (continued).

Matrix	Method	Instrument		Sampling procedure	Contaminants determined	C_{min}	Ref.
		name	manufacturer				
Tantalum, Ta_2O_5, $Ta(OEt)_5$	MS	SPQ 8000	Seiko Instruments Company	dissolution in a mixture of HF and HNO_3, for tantalum oxide, in an autoclave, dilution with H_2O. Separation of the sample matrix on an ion-exchange column (Dowex 1-X 8)	Be, Al, Ti, Cr, Ni, Nb, Mo, Sn, W, Th, U	0.003 – 0.02 ng ml^{-1}	10
Platinum	AES	ICPQ-1015	–	dissolution in aqua regia, concentration with addition of HCl, dissolution of the dry residue in 10% HCl	Mg, Mn, Cu Ag, Fe, Zn, Au Ir, Ni, Pb, Rh, Al Pd	1×10^{-4} mass %, 3×10^{-4} mass %, 5×10^{-4} mass %, 8×10^{-4} mass %	8
	MS	ELAN 6000, CETAC LSX-200	Perkin Elmer, Cetac Technologies	laser ablation	Rh, Ag, Pd, Hf , Ir, Pb, U Co, Ni, Cu, Zr, Ru, In Sn	$n \times 10^{-7}$ mass %, $n \times 10^{-6}$ mass %, $n \times 10^{-5}$ mass %	31
Silver	MS	ELAN 5000	Perkin Elmer	dissolution of sample (1g) in 7 M HNO_3, matrix precipitation in the form of AgCl	Al, Co, Pb Mg, Mn, Ni, Cu, Cd, Sn, Au Fe	$n \times 10^{-10}$ mass %, $n \times 10^{-9}$ mass %, $n \times 10^{-8}$ mass%	63
	MS	ELAN 6000, Laser Sampler Model 320	Perkin Elmer	laser ablation	Zn, Cd, Sn, Sb, Au, Pb, Bi	$n \times 10^{-4}$ mass %	57
Gold	MS	ELAN 5000	Perkin Elmer	dissolution in aqua regia, electrochemical precipitation of the sample matrix	Be, Mg, Cr, Mn, Ni, Cu, Zn, Ag, Pd, Sn, Pb	$n \times 10^{-6}$ mass % – $n \times 10^{-5}$ mass %	78
	AES	JY385	Jobin Jvon	dissolution in aqua regia, concentration, dissolution of the residue in 6 M HCl	Ag, Cd, Cr, Cu, Fe, Mn, Ni, Bi, Co, Pb, Pd, Sb	$n \times 10^{-5}$ mass % – $n \times 10^{-4}$ mass %	62
	MS	–	–	–	44 contaminants	0.0006 – 0.21 mg $litre^{-1}$	51
	MS	Model 7500	Agilent Technologies	dissolution in aqua regia. Dilution to 0.1% gold solution	29 contaminants	$n \times 10^{-8}$ mass % – $n \times 10^{-5}$ mass %	64
Zinc	AES	–	–	microcolumn preconcentration with DCS-arsenazo in a flow system	REE	n /ng ml^{-1}	79
	AES	–	–	dissolution of sample (1g) in a mixture of H_2SO_4 and HNO_3, extraction of analytes into xylene, as diethyldithiocarbamate complexes, reextraction into HNO_3	Cu, Ag, Cd	7×10^{-6} mass % – 1×10^{-5} mass %	80
Uranium	MS	ELAN 6000	Perkin Elmer	sample of 0.5 g. Separation of uranium on an extraction chromatographic column with the use of tributyl phosphate	26 contaminants	$n \times 10^{-8}$ mass % – $n \times 10^{-5}$ mass %	81
Iron	AES	Monochromator P-5200	Hitachi	dissolution of a sample (2g) in HCl, co-precipitation of analytes with cupferon, dissolution of the precipitate in a mixture of H_2SO_4, HNO_3 and $HClO_4$, addition of HF, concentration, dissolution of the salts in tartaric acid	V, Hf, Mo, Nb, Ga, Zr, Ti	3×10^{-6} mass % – 9×10^{-5} mass %	56
	AES	–	–	dissolution in a mixture of H_2O_2 and HF, ion-exchange preconcentration	Mo, W, Nb, Ta	–	82
	AES	–	–	dissolution of a sample (1g) in a mixture of HNO_3 and HCl with addition of acetic acid. Sorption of contaminants on DDTC. Elution with a mixture of HNO_3 and H_2O_2	Bi, Pb, Ni, Co	3×10^{-8} mass % – 9×10^{-7} mass %	83

Table 1 (continued).

Matrix	Method	Instrument		Sampling procedure	Contaminants determined	C_{min}	Ref.
		name	manufacturer				
Iron	AES	UOP-2 MARK II, ultrasonic nebuliser	Kyoto Koken Precision Instruments Incorporation	dissolution of a sample (1g) with heating in HCl (1 : 4). Co-precipitation of analytes with cupferon, separation of the precipitate, dissolution in HNO_3 (100 ml)	Ti, V, Zr, Nb, Mo, Ta	3×10^{-7} mass % – 1×10^{-5} mass %	65

[a] Beijing Broadcast Equipment Factory (China) self-made similar to HGA 500 (Perkin Elmer).
Note. Here and in Table 2, the papers originally published in Chinese or Japanese are cited from the abstracts in *Chemical Abstracts*. The dash means that the abstract contains no data.

Table 2. Methods of analysis of rare-earth oxides by ICP-AES and ICP-MS.

Matrix	Method	Instrument		Sampling procedure	Contaminants determined	C_{min}	Ref.
		name	manufacturer				
Yttrium oxide	AES	LABTEST	Labtest Equipment Company and others	dissolution in HNO_3 . Extractive chromatographic separation of the matrix from the analytes, preconcentration of the solution	up to 30 contaminants, including REE	$n\times10^{-5}$ mass % – $n\times10^{-1}$ mass %	16, 60, 84, 85
				fluorination of a sample with polytetrafluoroethylene in ETA	the same	$n\times10^{-2}$ – n ng	16
Lanthanum oxide	AES	Spectrograph	Beijing Instruments Factory	dissolution in $HNO_3 + H_2O_2$. Chromatographic separation of the matrix and the analytes, introduction of the eluate into the ETA	REE	0.8 – 48 ng ml^{-1}	14
	AES	Chromatograph	Shimadzu	preconcentration of impurities on a C – Si-gel in a flow microcolumn system	Non-REE impurities	$n\times10^{-1}$ mass%	86
	MS	POEMS II ELEMENT, chromatographs	Thermo Jarrell Ash Finnigan MAT, Shimadzu	dissolution in HNO_3. Separation of the matrix from impurities by high-performance liquid chromatography	REE	$n\times10^{-10}$ mass % – $n\times10^{-8}$ mass %	36, 87
Cerium oxide	AES	Spectrograph PGS-2, HPLC system	Karl Zeiss Jena Shimadzu	dissolution of a sample (0.1g) in $HNO_3 + H_2O_2$. Chromatographic separation of the sample matrix and the analytes, introduction into the graphite ETA	REE	0.8 – 36 ng ml^{-1}	15
	AES	LABTEST	Labtest Equipment Company	extractive chromatographic separation of the matrix and the analytes	REE	5×10^{-5} mass % – 5×10^{-3} mass %	61
	MS	–	–	dissolution in HNO_3	Gd, Tb, La, Pr	0.008% overall	88
Neodymium oxide	MS	HP 4500	Agilent Technologies	0.01% solution of neodymium oxide in 0.1% HNO_3	La, Ce, Pr, Sm, Eu, Gd	$n\times10^{-5}$ mass % – $n\times10^{-4}$ mass %	59
Samarium oxide	AES	–	–	dissolution in HNO_3. The concentration of Sm_2O_3 in the solution is 5 mg ml^{-1}	Cu, Fe, Ca, Ni	3×10^{-4} mass % – 3×10^{-3} mass %	89
Europium oxide	AES	–	–	microcolumn preconcentration in a flow system	Al, Cr, Cu, Fe, Pb, V, Zn	n ng ml^{-1}	90
	AES	–	–	concentration on an active Si – C-gel in a flow regime	Al, Cr, Cu, Fe, Pb, V, Zn	–	91
	AES	–	–	extraction of impurities	REE, Cu, Pb, Co, Ni	7×10^{-4} mass % – 7×10^{-2} mass %	92
Europium, europium oxide	MS	–	–	dissolution in HNO_3	Cr, Mn, Co, Ni, Cu, Cd, Pb	0.12 – 0.3 mg litre^{-1}	53
	MS	–	–	–	REE	0.005 – 0.02 ml litre^{-1}	55
	MS	–	–	chromatographic separation	REE	0.001 mass % – 0.015 mass %	93

Table 2 (continued).

Matrix	Method	Instrument		Sampling procedure	Contaminants determined	C_{min}	Ref.
		name	manufacturer				
Gadolinium oxide	MS	VG Plasma Quad	VG Elemental	dissolution in 50% HCl. Concentration. Dissolution of the residue in 1% HCl. Chromatographic separation of La, Ce, Pr, Nd, Sn, Eu and the major part of Gd	Tb, Tm, Yb, Lu	2×10^{-7} mass % – 5×10^{-6} mass %	54
Terbium oxide	AES	–	–	separation of the matrix from the analytes by HPLC	Ca, Cu, Mg, Mn, Ni, Si, La, Ce, Pr, Nd, Sn, Eu, Gd	0.04 mass % – 0.4 mass %	94
Dysprosium oxide	MS	–	–	dissolution in HNO_3	REE	0.01 – 0.09 mg litre^{-1}	52
REE oxides	AES	Spectrograph PGS-2	Karl Zeiss Jena	dissolution. Concentration of impurities on an active C – Si-gel in a flow microcolumn system	Al, Cr, Cu, Fe, Pb, V, Zn	1 – 10 ng ml^{-1}	95

VII. Conclusion

The main advantages of ICP as the ion source in mass spectrometry and the radiation source in atomic emission spectroscopy for the analysis of high-purity solids are as follows:

— relatively easy combination with different sample introduction systems (solution nebulisers, graphite atomisers, laser and spark ablation);

— multielement analysis with low element detection limits;

— plasma stability, which provides the reproducibility of the analytical signal;

— simple calibration (in the analysis of solutions);

— small non-spectral matrix effects.

Let us also denote the drawbacks of ICP:

— the necessity of dissolution of a sample, which may lead to uncontrolled introduction of contaminants, especially common ones, and to the risk of losses of the analytes;

— low capacity, usually not higher than 2 kW, which results in plasma instability in the case of direct introduction of powders and suspensions;

— formation of a great variety of molecular ions, which increases the element detection limits by ICP-MS due to interferences, especially in the mass range from 25 to 80 a.m.u;

— high cost of the equipment, especially for mass spectrometric analysis.

The record-breaking low absolute detection limits (down to 10^{-14} g) that can be provided by multielement ICP-MS on a double-focusing instrument with introduction of 0.05% – 0.2% solution of a sample (or a concentrate) into the plasma, make it possible to reach detection limits of 10^{-9}% – 10^{-7}% without concentration and down to 10^{-11}% – 10^{-9}% with virtually complete sample matrix separation for non-common contaminants the analytical lines of which are free from molecular ion overlap. The detection limits for the elements in the mass range from 24 to 80 a.m.u. and for a number of rare-earth elements in REE-containing matrices (neodymium, europium, cerium) are several orders of magnitude larger (10^{-6}% – 10^{-3}%). The element detection limits in the direct analysis of solids by LA-ICP-MS lie generally in the range 10^{-7}% – 10^{-5}%, and the use of powerful IR laser reduces the limits to 10^{-10}% – 10^{-7}%. It should be noted that ICP-MS covers a broad range of analyte detection limits.

In the majority of published works, the analyte detection limits with ICP-AES on echelle spectrometers with introduction of 1% solutions into the plasma are no lower than 10^{-6}% – 10^{-4}% for direct analysis and 10^{-8}% – 10^{-5}% for the method with preconcentration. It is obvious that low detection limits of trace-elements in the matrices with multilinear spectra (d- and f-elements) require the sample matrix to be separated. The use of ultrasonic nebulisers, instruments with an axial observation of plasma [65], and ETA also reduces the detection limits.

Considering multielement analysis, both methods allow simultaneous determination of several tens of contaminants in pure substances. However, according to the published works, usually no more than ten elements were determined. Determination of several tens of impurities simultaneously at the level of 10^{-7} mass % – 10^{-6} mass % and non-common elements with a detection limits as low as 10^{-11} mass % (see [35]) by ICP-MS represents an exception. [9, 11–13, 35] The limited number of contaminants that can be determined is often explained by the purposes of the study (for example, in the graphite nuclear reactor, only neutron-absorbing REE were determined),[27] and by the capacities of the concentration procedures.

Inductively coupled plasma atomic emission spectroscopy and mass spectrometry supplement each other, and their parallel use for the characterisation of high-purity substances allows verification of the correctness of the analysis by methods different in principle, and determination of the elements the analytical lines of which in one of the methods are hidden by spectral overlaps.[9, 11, 70] In other words, due to the multielement nature and low detection limits, the combination of the two methods makes it possible to fully characterise a high-purity substance regarding virtually all elements from the Periodic Table, excluding the gaseous ones. For the analysis of certain high-purity compounds by ICP-MS, see also Refs 3, 6, 7 and 46.

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