



UTILIZATION OF ATOMIC EMISSION SPECTROSCOPY METHODS FOR DETERMINATION OF RARE EARTH ELEMENTS

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The intensive priority of utilization of the rare earth elements (REE) has started since seventy years. The great importance of high purity compounds of REE has found their utilization first of all in electrical industry, nuclear energetics, optics, ceramics, engineering, chemical industry and other. The importance of data on REE for petrogenetic classification of rocks since it provides information on magma differentiation and the metamorphic or other geochemical processes is well recognized [1]. The new analytical techniques and procedures which were developed in eighties for determination of ultra-trace contents of REE have led to their wide popularization not only for many geochemical and petrogenetic investigations but for the environment monitoring as well. Requests for REE determination have therefore become common in most geoanalytical laboratories in spite of the fact that analysis of usual concentration levels is in the least not a simple task.

Many years ago only two analytical techniques, namely neutron activation analysis (NAA) and isotope dilution mass spectrometry (IDMS), were available for the determination of REE at chondritic abundance levels in rocks and minerals, but use of these techniques remained confined to a few well-established laboratories, mainly because of the high cost of the equipment. In the seventies, inductively coupled plasma (ICP) spectrometry had a great impact in this field in its optical version and more recently in its ICP-MS form [2-4].

Despite considerable progress in REE determination as witnessed by numerous publications, several problems have still remained and may cause errors if not properly handled. Problems in the determination of REE arise from their very low concentration in many common substances (rocks, ores, slags) as compared to the concentration of main elements.

Most of matrix elements falsify the REE determination by ICP-AES because of spectral overlaps and background continuum interferences [5]. In most cases, REE group separations are required prior to analysis to eliminate or minimize interferences with concomitant elements, such as Fe, Al, Ca, Ti, and to increase the sensitivity. Additional, optical spectra of some of the REE are fairly line-rich with many overlaps and coincidences. Mutual spectral interferences are therefore fairly common, and they are highly instrument dependent. To achieve correct analytical results, extensive experimental work with the particular used instrument and with regard to the expected composition of the analyzed samples is required.

The next serious problem of reliable determination of REE in geological materials consists in incomplete dissolution of the sample. Some of the REE may be bound in accessory minerals which may not be properly attacked by the mixture of acids, including HF, generally used for decomposition. An incomplete decomposition may even result in a fractionation of the REE, thus changing their mutual ratios. Decomposition, therefore, should proceed in two steps: after digestion with acids, an alkali fusion of the undissolved residue should be included.

The application of ICP-AES method for detection sometimes needs a chemical separation and enrichment step to achieve the required detection limits and elimination of interferences. Separation of REE by precipitation yields in unacceptably high matrix salt load, by coprecipitation with Ca oxalate or CaF₂ the losses may occur through the formation of colloid solutions or soluble REE complexes, whereas liquid-liquid extraction and separation by ion exchange procedures proved to be suitable for a following ICP analysis. Any of these methods are not free from limitations (e.g. loss of REE during separation of matrix elements).

In our laboratory we have been involved in the problems of REE determination since 1977. We elaborated and applied procedures for REE determination using optical emission spectrography with D.C. arc excitation and ICP atomic emission spectrometry.

REE determination by methods of atomic emission spectrography

We worked out a reliable, simple, fast and economically advantageous method for REE determination in different minerals (titanites, apatites, epidotes, garnets, scheelites and turmalines), consisting in the transformation of REE in their heavily soluble fluorides [6,7]. Owing to the lowest solubility of REE fluorides, as compared with their other compounds, this procedure ensures a sufficient quantitative separation of the analyzed elements precipitated together only with Ca (and Li) contained in the original sample. The problem of the analysis of different minerals was so restricted to the REE determination in practically pure CaF_2 matrix. The REE are so separated and simultaneously enriched in a single common matrix what enables to prepare calibration standards for the analysis of different types of geological materials only in CaF_2 . The most sensitive REE spectral lines are in UV and VIS spectral region a part of which is covered with intensive cyanogene bands. For to suppress their influence we worked in CO_2 protective atmosphere using Schöntag's quartz cuvette. The greatest interest was dedicated to the choice of analytical spectral lines applicable from the point of view of their mutual interferences and interferences caused by high Ca concentration.

REE determination by ICP-AES

For the solution of several geological problems requiring data on REE contents, the reliability and in particular the detection limits of results obtained by the above mentioned method were not satisfactory. Many disadvantages of the classical excitation sources are significantly suppressed by the application of inductively coupled plasma. Among the main advantages of this excitation source as applied for REE determination, good detection limits for the majority of the analyzed elements, elevated precision and relatively simple background have to be quoted. The necessity to dissolve solid materials and the presence of often significant mutual and matrix interferences, representing the main sources of errors at the REE determination, have to be considered as the principal drawbacks of ICP application.

In our laboratory we have used different decomposition procedure according to the type of the analyzed material. For the decomposition of rocks, repeated treatment with acid mixture ($\text{HNO}_3 + \text{HF} + \text{HClO}_4$) and following fusion of the insoluble residue with NaBO_2 has been most often applied. From the solution prepared on the indicated way the separation of REE is performed by means of catex ion exchanger Dowex AG 500W-X8 [8]. A disadvantages of the separation proposed in this procedure consists in the great volume of relatively concentrated acid necessary for the elution (400 ml 1.8M-HCl and 450 ml 6M-HCl) which must be evaporated for the final adjustment of the resulting solution. This essentially increases the laboriousity and duration of the analysis, even not speaking about the loading of the environment.

An essential part of the experimental work at the elaboration of the procedure for REE determination is played by the choice of analytical lines and determination of appropriate correction factors for the elimination of still present interference influences. Despite the separation of REE concomitants their mutual interferences however not be avoided. The calculation of correction factors must be performed for each used technique, it is namely not possible to take their values simply from literature. The proposed procedure was applied for the analysis of different types of geological materials from several Slovak localities. The results

the REE determination were used for e.g. investigation of REE distribution in volcanic rocks, rhyolite tuffs with U-Mo mineralization, sandstones with heavy minerals accumulations, phosphatic sandstones, granites, quartz-carbonate veins [9] and in the meteorite found in the locality Rumanová.

REE determination in mineral waters

Mineral waters are characterized by a relatively large variability in their basic chemical composition and their REE contents are very low as compared with the concentrations of main components. From these reasons the use of separation-preconcentration procedures is in the majority of cases inevitable. In a collaboration with Dr. Nevorál [10] who determined REE in mineral waters after their separation and preconcentration spectrophotometrically, we analyzed the same samples using ICP-AES. REE contained in mineral waters from Czech Republic (taken volume 25 - 100 l) were preconcentrated and separated by means of the ion exchanger Dowex 500W X12. For spectrophotometric determinations the REE elution from a column with catex Dowex 50W X8, ammonium salt of α -hydroxyisobutyric acid at pH 4.43 of increasing concentration was used. For the final determination of Sc 4-(2-tiazolylazo) resorcinol, for the other RE xylenol orange in the presence of cetylpyridinium bromide was used.

The REE contents were determined in 19 mineral water sources and the results obtained by the both mentioned methods compared. The total REE contents in the analysed mineral water samples were between 2×10^{-7} and 3×10^{-5} g dm⁻³. The obtained results were used for the characterization of the mineral water springs, and the mutual correlations of the REE contents served as a basis for hydrogeochemical evaluation of rock-water interactions.

Conclusion

The perspectives for improvement of REE determinations using methods of atomic emission spectroscopy can be found first of all in the region of sample treatment e.g. in the use of more effective separation and preconcentration procedures. Application of the described methods (classical fluoride precipitation and ionex chromatography) cannot ensure a sufficiently high preconcentration factor for all REE (problems connected with the decomposition of high sample inweights, limited sorption capacity of ion exchangers etc.). The application of ionex chromatography is laborious and extremely time consuming. From this point of view, so called chelating ion exchangers Ostsorb-Arzenazo (OA) and Spheron-Salicyl (SS) of Czech production are more perspective. These exchangers have a high selectivity on the REE, at the found pH=6 the efficiency of REE sorption is in the range 98.3-104.6%. The OA sorbs only Fe from a model solution containing Al, Fe, Mn, Ca, Mg, K, Na, but at the specific condition (masking, application of multifunctional buffering solution for Al and Fe) the sorption of Fe can be prevented. The SS sorbs besides REE quantitatively also Al and Fe depending upon the capacity of chelating ion exchanger. At the use of static procedure which is simpler than the dynamic one, the efficiency of REE sorption in the range 95-105% was found. The preconcentration and separation procedure based on the mentioned chelating ion exchangers has till now been proved only on model samples but on the basis of the gained results it is possible to state that it represents an essentially more effective preconcentration-separation method than the till now used ones.

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