

INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION-SPECTROSCOPY OF LANTHANIDES IN SILICATES

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ABSTRACT. — The determination of Rare Earth Elements (REE) by inductively coupled plasma atomic emission spectroscopy is discussed. The spectral interferences due to the major, minor and trace elements present in the common silicate matrices are showed.

The possibility to overcome some of these effects by operating through spectral parameters is outlined. The overcoming of major elements interferences by an ion-exchange separation is also discussed.

RIASSUNTO. — Nel presente lavoro viene discussa la possibilità di determinare il gruppo degli elementi appartenenti alle Terre Rare mediante spettroscopia in emissione utilizzando come sorgente di eccitazione una torcia a plasma. Questa è in grado di aspirare campioni allo stato liquido, impiegando un flusso di argon che viene ionizzato mediante impulsi a radio frequenza e riscaldato a temperature dell'ordine dei 10.000° C, con conseguente miglioramento delle caratteristiche di emissione e di sensibilità specie nella determinazione di elementi refrattari, quali i lantanidi, che normalmente non possiedono limiti di detezione apprezzabili con altre tecniche spettrochimiche.

Essendo state riscontrate forti interferenze spettrali dovute alla presenza di elementi come ferro, sodio e calcio, nella matrice silicatica delle rocce e dei minerali comunemente studiati, viene proposta una separazione dalla matrice dell'intero gruppo delle terre rare mediante resine a scambio ionico.

Vengono inoltre studiate le possibili interferenze tra questi elementi e mostrate alcune possibili variazioni nella scelta delle lunghezze d'onda analitiche ai fini di una migliore determinazione. Viene infine evidenziato come sia possibile, in caso di necessità, determinare senza interferenze gli elementi del gruppo delle Terre Rare, anche se simultaneamente presenti.

Introduction

Plasma is physically defined as « an electrically neutral, highly ionized gas composed of ions, electrons and neutral particles ». In most applications of emission spectroscopy the gas is a stream of argon, which is ionized by the influence of a strong electric field, either a direct current or at radio frequency (i.e. the inductively coupled plasma or ICP). The discharge causes the flowing argon gas to become electrically conducting, and heats it to a high temperature, with a maximum somewhere between 7000 and 15.000° C (FASSEL & KNISELEY, 1974 a and 1974 b; SCOTT et al., 1974; GREENFIELD et al., 1975, 1976). At such elevated level of temperature the sensitivity of refractory elements such as rare earths (REE), yttrium, zirconium, niobium etc., is enhanced particularly if compared with traditional spectrochemical techniques such as electrothermal atomic absorption spectrophotometry.

The determination of REE have become more and more important in science and industry. Indeed, the study of their concentration and distribution in rocks and minerals is a powerful tool in the study of the geochemical processes. From a technological point of view, REE have found an increasing interest, for instance, in the manufacturing of

high quality steels. Consequently, analytical techniques having a high detection power for REE are required.

The analytical problems in the determination of the lanthanides in terrestrial rocks are considerable. The most widely method at present would appear to be neutron activation analysis (GORDON et al., 1968; VOLDET & HAERDI, 1978; WHITLEY et al., 1979). The alternative to neutron activation include isotope dilution mass spectrometry (HOOKER et al., 1975) and spark-source mass spectrography (STRELOW & JACKSON, 1974; TAYLOR & GORTON, 1977). All these techniques have both advantages and disadvantages, but few would dispute the desirability of investigating alternative methods of analysis such as electrothermal atomic absorption spectrophotometry (MAZZUCOTELLI & FRACHE, 1981) or high performance liquid chromatography (MAZZUCOTELLI et al., 1982).

Inductively coupled plasma atomic emission spectrometry has been shown to have considerable sensitivity for the measurement of lanthanides (BROECKAERT et al., 1979; NIKDEL et al., 1979). WALSH and co-workers (1981) describe an ICP procedure applied on rock solutions before a previous separation performed on cation exchange resins. These authors, however, don't describe the encountered interferences in the spectral treatment of used emission lines. The present paper describes some spectral interference effects and the technique used to overcome these ones.

Experimental

Sample dissolution

Weigh out 0.3000 ± 0.001 g of finely powdered (130 mesh) sample in a pure nickel crucible. Add about 1.5 g of sodium peroxide and mix. Add another 1.5 g of sodium peroxide as a thin layer over the sample. Fuse on an asbestos board over a bunsen burner to a black liquid melt. Let the crucible cool, clean the outside with hot .6 M hydrochloric acid to obtain a clear solution. Use the mixture to rinse the crucible; the final volume of the sample solution would be as small as possible, containing hydrochloric acid to have a final concentration of .6 M about.

Column packing

Fill a borosilicate glass tube (15 mm bore, with fused — in porosity — 3 glass sinter and Teflon burette tap at the bottom) with Dowex 50W-X8 resin (200-400 mesh, strongly acidic form) to give a column height of 180 mm, and wash it with 300 ml of 3 M hydrochloric acid. Wash with water until free from any acid reaction. Adjust the flow rate to 3.0 ± 0.5 ml/min. Pretreat the column with 30 ml of .6 M hydrochloric acid.

Analytical procedure

Pass the solution obtained after the sample dissolution carried out as above described through the ion-exchange column. Elute the matrix elements (Na, K, Al, Fe, Ti, Ca, Mg and some Sr) with 300 ml of 3 M hydrochloric acid in 25 % ethanol solution. Elute the REE group (plus Ba, Sc, Y and the rest of the Sr) with 200-250 ml of 6 M hydrochloric acid. If necessary evaporate this eluate to less than 100 ml in a Teflon beaker, then dilute to 100 ml in a standard flask. Use this solution for ICP measurements, with the parameters shown in tables 1 and 2.

TABLE 1
Operating parameters for REE determination on the ICP spectrometer

Plasma Gas Flow.....	15 L/min
Nebulizer Gas Pressure.....	20-40 psi
Forward rf Power.....	1250 watts
Reflected rf Power.....	5 watts
Plasma Viewing Height.....	15 mm
Slit setting.....	0.02 nm Low
Readout mode.....	Continous
PRINT Key.....	OFF
SCAN Rate.....	0.05 nm/min

Quantitative determinations have been carried out by aspirating in ICP torch solutions of mixed lanthanides at the same concentration level of the sample analyzed. The lanthanides mixture was obtained by adding the appropriate amounts of pure oxide solution. The oxide solutions were obtained by dissolving the pure REE oxides in hot hydrochloric acid and diluting to reach to a final concentration of .6 M HCl about; cerium oxide only was dissolved in sulphuric acid.

TABLE 2
Operating wavelengths for REE determination on the ICP spectrometer

Element	Used Wavelength (nm)	Relative Intensity	Other more sensitive Wavelength (nm)
La	379.48 (II)	3900	394.91 (9000 II)
Ce	418.66 (II)	3500	253.20 (20000 II); 350.46 (60000 I)
Pr	422.50 (II)	3800	417.94 (5200 II); 595.60 (7000 III) 414.31 (2700 II)
Nd	406.11 (II)	4700	450.36 (5400 II)
Sm	359.26 (II)	4200	388.53 (3700 II); 392.80 (1900 II)
Gd	364.62 (II)	6100	376.84 (8700 II)
Tb	350.92 (II)	5700	
Tm	346.22 (II)	8500	409.42 (10000 II); 248.94 (30000 III)
Eu	381.97 (II)	39000	420.50 (60000 II)
Dy	353.17 (II)	22000	
Ho	345.60 (II)	16000	
Yb	328.94 (II)	18000	369.42 (36000 II)
Er	349.11 (II)	6700	400.80 (14000 II); 429.01 (40000 III)
Lu	261.54 (II)	18000	
Y	371.03 (II)	13000	294.60 (99000 III)
Sc	361.38 (II)	28000	

Discussion and conclusion

The strong emission lines of the elements in ICP atomic spectroscopy are all referred to wavelengths referred to the emission of the considered elements: the contrary of what considered in classical spectrography where the analytical lines were referred to emissions of neutral atoms. In ICP spectroscopy the checking of analytical lines suffers from some kinds of considerations due to the possible spectral interferences of analytical lines with other strongly emitting radiations. For these reasons the analytical lines are not always the most sensitive lines.

To investigate these effects we have analyzed the spectral influence of the whole REE, the alkaline-alkaline earth and the iron influence on the analytical lines of single rare earth.

For example, fig. 1 shows the interference due to high amount of lanthanum on the analytical wavelength of gadolinium.

The draw reported in this figure reports the video-track of the ICP data station; the vertical line corresponds to the checked analytical wavelength while the entire drawing is referred to a 0.5 nm scanning. Fig. 1 shows the neighbour of the lanthanum emission line due to the single ionized atom: the high

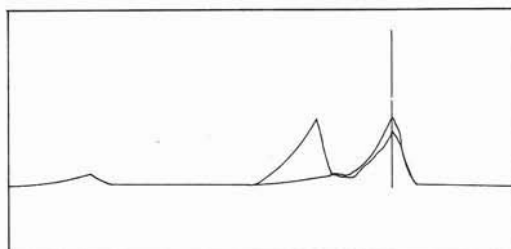


Fig. 1. — Spectrum around the wv. 364.60 nm. (vertical line) of Gd in presence of high amount of La.

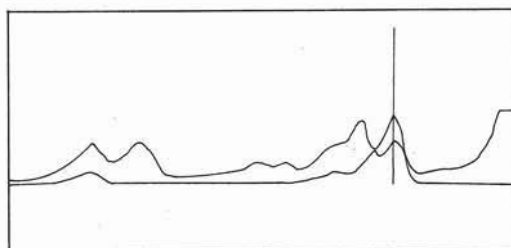


Fig. 2. — Spectrum around the wv. 364.60 nm. (vertical line) of Gd in presence of iron matrix.

La concentration (1000 ppm about) causes slight interferences by depressing the gadolinium line of 10% about of intensity; however the considered lanthanum/gadoli-

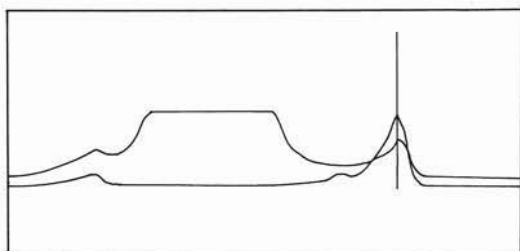


Fig. 3. — Spectrum around the wv. 364.60 nm. (vertical line) of Gd in presence of Na + Ca matrix.

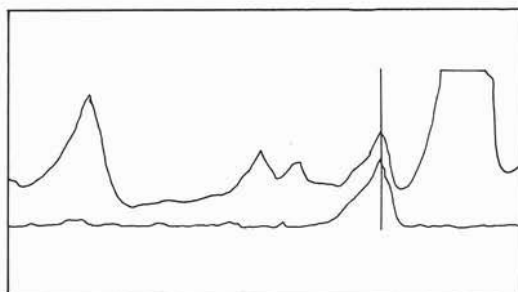


Fig. 5. — Spectrum around the wv. 392.80 nm. (vertical line) of Sm in presence of REE mixture.

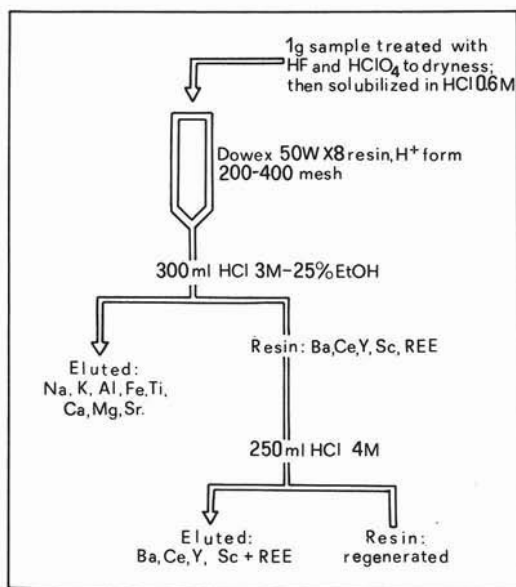


Fig. 4. — Separation scheme of REE.

nium ratio is surely very high when the matrix of common silicate rocks is considered.

Figures 2 and 3 show the same interfering effects on the 364.60 nm analytical line of gadolinium: in this case the depressing effect of 50 % about is stressed by the fact that the considered matrix/gadolinium ratio (1000 about) is considerably low than that encountered in natural geological samples.

Fig. 4 shows the ion-exchange separation scheme, early performed and derived from a more general procedure (MAZZUCOTELLI & FRACHE, 1981; MAZZUCOTELLI et al., 1976).

As showed, the accompanying elements of the whole lanthanides group are yttrium, scandium and barium. To investigate the possible interferences of these ions between them, the analytical lines of the single REE

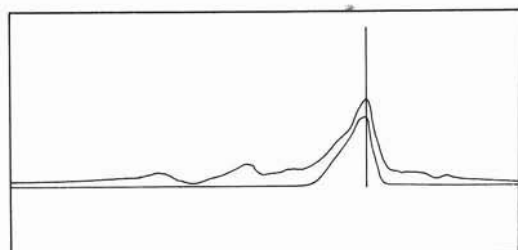


Fig. 6. — Spectrum around the wv. 359.26 nm. (vertical line) of Sm in presence of REE mixture.

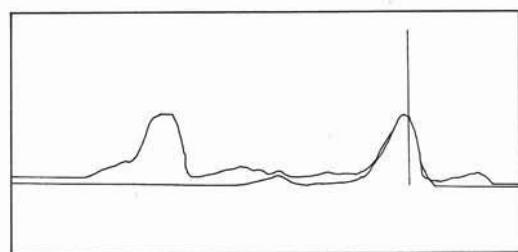


Fig. 7. — Spectrum around the wv. 418.66 nm. (vertical line) of Ce in presence of REE mixture ($\times 1$).

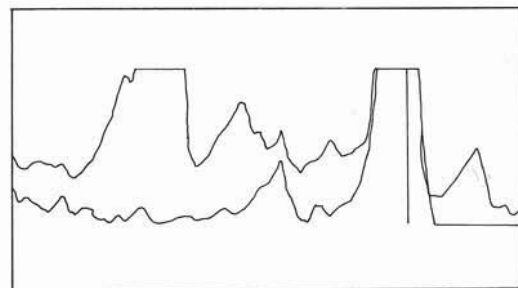


Fig. 8. — Spectrum around the wv. 418.66 nm. (vertical line) of Ce in presence of REE mixture ($\times 6$).

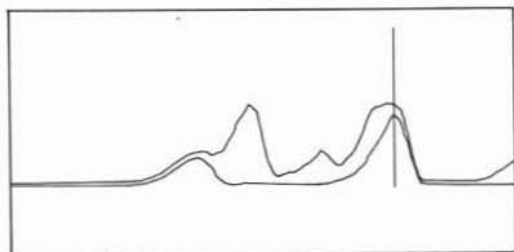


Fig. 9. — Spectrum around the $wv.$ 414.31 nm. (vertical line) of Pr in presence of REE mixture.

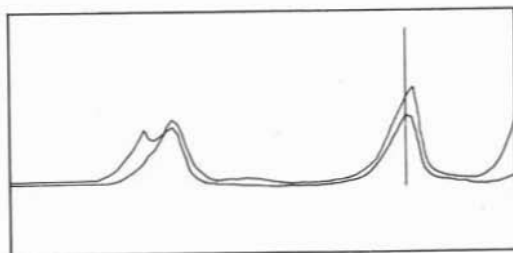


Fig. 10. — Spectrum around the $wv.$ 422.50 nm. (vertical line) of Pr in presence of REE mixture.

were scanned in presence of a mixture of all these elements.

Figs. 5 and 6 show the interference of REE mixtures on the samarium line 392.80 nm and its spectral overcoming by checking another wavelength such as 359.26 nm.

Figs. 7 and 8 show an expansion of the spectral background around the cerium analytical line of 418.66 nm.

Finally figs. 9 and 10 show, as considered

for samarium, a spectral interferences overcoming for the analysis of praseodimium.

In conclusion we think that an analytical procedure may be performed after a major elements separation and an ICP spectrometry of the lanthanides mutually present; however we think that an accurate study of the possibilities offered by the spectral adjustment may be of interest for the evaluation of a rapid method of analysis of rare earth elements.

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