

## Emission spectrographic monitoring of the effluent fractions from the ion exchange chromatography of silicate rocks

For the purpose of estimating several trace elements in silicate rocks, the combined use of ion exchange enrichment (anion and cation) and d.c. arc spectrochemical analysis has been investigated<sup>1-10</sup>. Before satisfactory conditions could be developed for the enrichment of trace amounts of Cs, Ce, La, Nd, Sc, Y, Sn, Mo and Ga by cation exchange chromatography with hydrochloric acid elution, studies were undertaken<sup>1</sup> to ascertain the sequence of movement of abundant (Na, K, Mg, Ca, Al, Fe, Mn and Ti) and trace (Ag, Ba, Be, Ce, Co, Cs, Cu, Ga, La, Li, Mo, Nd, Ni, Pb, Rb, Sc, Sn, Sr, Tl, V, Y, Zn and Zr) constituents of silicate rocks through cation exchange columns under different experimental conditions. Reference rocks, granite G-I and diabase W-I, and the collected data on these two rocks were used extensively in these investigations<sup>11-13</sup>.

Emission spectrography was used to monitor the effluent fractions obtained from the cation exchange columns. The spectrograph was useful because the spectrum of each fraction provided a permanent and fairly complete record of its composition. Unlike other monitoring procedures, emission spectrography was ideally suited for the simultaneous detection of several elements in each effluent fraction. A measure of the concentration of an element in the fractions could be readily obtained by visually estimating the relative intensity of a suitable spectrum line of the element (a sensitive line was used for trace constituents and a line of lesser sensitivity was employed for major constituents) in the spectrograms. The determinations for individual elements were used to construct semiquantitative elution curves representing the flow of the elements from the column<sup>1</sup>. Visual inspection of the spectrograms readily revealed the beginning, maxima and end of the elution of a particular element.

Emission spectrographic monitoring of the column effluent has been used by EDGE<sup>14,15</sup> and FARIS AND WARTON<sup>16</sup> to examine the adsorption of rare earths on strongly basic anion exchange resins from nitric acid-aliphatic alcohol media; by FARIS<sup>17</sup> to examine the adsorption of rare earths on Dowex 1 from mixed solvents containing  $\alpha$ -hydroxy-isobutyric acid and by FARIS<sup>18</sup> to study the adsorption of some 50 elements on a strongly basic anion exchange resin from 1 *M*-24 *M* hydrofluoric acid.

### *Experimental*

#### *Spectrographic monitoring of effluent fractions*

For monitoring purposes, 10-20 ml fractions of effluent were collected on an automatic fraction collector and taken carefully to dryness in 45 ml vitreosil basins.

The following spectrographic conditions were employed for examining the effluent fractions:

*Electrodes.* Flat topped and 2.4 mm (internal diameter)  $\times$  3 mm (depth) cavity electrodes were cut from National Carbon Company special grade 3/16 in. graphite rod. These electrodes were used as the lower electrode (anode). The upper electrode (cathode) was a pointed Ship Carbon Company S.G. 305-H 0.5 mm diameter carbon rod.

*Loading electrodes.* Electrodes were held in plastic tweezers during loading. Flat topped electrodes were rubbed with a circular downward movement around the

bottom and sides of the vitreosil basins containing very small amounts of residue in order to obtain as complete a transfer as possible of the material onto the electrode surface. Cavity electrodes were loaded by pressing the cavity into the material in the dish. This process was repeated until the cavity had been filled. When moderately large amounts of material were present, the cavity was pressed into different areas of residue. Smaller quantities of residue were first scraped into a heap in the centre of the basin with the aid of the electrode. Hygroscopic and deliquescent residues were dried prior to loading and arced as soon as possible afterwards. Two electrodes were loaded per basin.

*Arcing conditions.* One electrode was arced to completion at 7 amps d.c. in the 2,800–5,000 Å wavelength region (the most sensitive lines of a large number of transition and non-transition elements fall in this wavelength region) and the other electrode was arced at 3 amps d.c. in the 4,500–9,000 Å wavelength range (alkali metals have their most sensitive lines in this region). To ensure that CN red emission was held to a fairly low level, exposures in the last wavelength range were not continued much past the apparent end of the total burn. Because of the small amount of material present in many electrodes, as well as the ready volatility of chlorides, care was taken to record the first few seconds of arcing by opening the shutter before striking the arc.

*Spectrograph.* Hilger (E 492) large quartz and glass; wavelength range 2,800–5,000 Å (quartz optics), 4,500–9,000 Å (glass optics); external optics Hilger F958 quartz lens focussed on slit; slit width 0.0025 mm; slit height 3 mm.

*Plates.* Kodak 103-0 plates were used for the 2,800–5,000 Å wavelength range and Kodak I-L plates were employed for the 4,500–9,000 Å region.

*Plate processing.* Plates were developed for 4.5 min in Kodak D19b developer at 20°.

*Spectral lines used for monitoring purposes.* See Table I.

TABLE I

## SPECTRAL LINES USED FOR MONITORING PURPOSES

Lines marked with an asterisk were used for plotting semiquantitative elution curves.

Element	Spectral line (Å)	Element	Spectral line (Å)
Ag	3382.89	Mn	4033.07*
Al	3082.16*	Mo	3170.35*
Ba	4554.04*	Na	5688.22*; 3302.99
Be	3131.07	Nd	4303.57*
Ca	4425.44*	Ni	3458.47*
Ce	4296.68	Pb	4057.82
Co	3453.51*	Rb	7947.60*; 4201.85
Cu	3247.54	Sc	4246.83*
Cr	4254.35*	Sn	3175.02*
Cs	8521.10*; 4555.36	Sr	4607.33*
Fe	2912.16*	Ti	3241.99*
Ga	4172.06*	Tl	3775.72
K	6938.98*; 4044.14	V	4379.24*
La	4333.73*	Y	4374.94*
Li	6103.64*; 3232.61	Zn	3345.02
Mg	3096.90*	Zr	3438.23*

*Construction of semiquantitative elution curves*

A semiquantitative measure of the concentration of an element in the effluent fractions was obtained by visually estimating the relative intensity of a suitable spectrum line of the element (see Table I) using an arbitrary 7-stepped spectrum line as a source of reference. Semiquantitative elution curves were constructed by plotting element relative intensities against effluent fraction number.

Reagent blank tests, carried through all the steps of the cation exchange and spectrographic analysis procedure, were made in all cases.

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