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**Electrothermal Atomisation for Atomic-Absorption Determination of Some Rare Earths in Silicate Rocks and Minerals**

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The most useful indicators of geochemical processes are groups of trace elements with very similar physico-chemical properties. The rare-earth elements (REE) may be considered the best available group of this type, because all have essentially the same chemical properties and display small regular differences in mass and also in ionic radius (as a result of the lanthanide contraction). Since the compositional trend of the REE has been widely used by several authors\(^1\) to investigate the evolution of igneous rocks, an accurate determination of lanthanide abundance is important in analytical chemistry related to geochemical work.

Most of the data on the REE contents of international rock and mineral standards have been obtained by radiometric techniques, such as instrumental and radiochemical neutron-activation analysis\(^5\)\(^–\)\(^7\). However, these techniques are expensive and not readily available. In order to devise an alternative and widely applicable technique we have studied the application of atomic-absorption spectrophotometry (AAS) with electrothermal atomisation to the rare-earth elements.

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Experimental

In previous work it has been shown that major, minor and trace elements in a common silicate rock matrix may interfere in the atomic-absorption determination of Eu, Yb, Dy, Ho and Tm. These five elements are considered to give the most sensitive response (of REE) when electrothermal atomisation is used.

The strongest interfering effect has been ascribed to the presence of major elements such as Ca, Fe, Al, Na and K. Minor and trace elements (including other lanthanides) give little interference, especially when they occur in low ratios to Eu etc., as in natural geological samples. For this reason the determination of these REE in dissolved rock samples is neither accurate nor reproducible. Moreover, Na and K appear to be the only elements of which the interfering effect may be overcome by changing the instrumental parameters, e.g. by increasing the ashing-stage temperature to 1800°C.

An ion-exchange separation from the matrix elements appears the best method of overcoming these interferences and determining the REE with accuracy and reproducibility.

As cited above, the low interference by some minor (Ba and Sr) and trace elements (Sc, Y and other REE) at the levels found in common silicate rocks makes it unnecessary to separate the individual lanthanides from these elements and from each other.

We can therefore apply the ion-exchange separation scheme described earlier which consists of a controlled acid attack (hydrofluoric, perchloric and 0.6 M hydrochloric acids) and subsequent separation on Dowex 50W X8 strongly acid ion-exchange resin. All the major and some minor elements are removed by elution with 3 M hydrochloric acid in 25% ethanol medium. The lanthanide group is then collected along with Sc, Y, Ba and part of the Sr by elution with 4 M hydrochloric acid.

Instrumentation

A Varian-Techtron AA 775 atomic-absorption spectrophotometer equipped with a CRA 63 carbon-rod electrothermal atomiser was used, with a Hewlett-Packard oscillographic recorder with memory storage.

Procedure

Weigh out 500.0 mg of finely powdered sample (120 mesh) in a PTFE dish. Moisten the powder with water to avoid spattering. Add 10 ml of 40% hydrofluoric acid and 10 ml of 70% perchloric acid, mixing with a platinum or PTFE rod. Allow to stand over-