of the extra solution influences the complexation reaction of ions to be separated with the eluting agent, the relative permitivity of the intra-solution affects the association of these ions with the active group. It can be supposed that equilibrium constants of these reactions differ considerably. The non-identical position of maxima on both curves is therefore not surprising. Nevertheless, the qualitative agreement of both curves seems to show out that the composition of the intra solution plays some role in the enhanced separation efficiency of mixed media and that the existence of three types of solutions in the system ion–exchanger, liquid phase can be accepted as probable.

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ON THE DETERMINATION OF STRONTIUM IN SILICATES, CARBONATES AND SULPHATES BY ATOMIC ABSORPTION SPECTROSCOPY

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Strontium is one of the elements that are frequently determined by atomic absorption spectroscopy. The sensitivity of the determination for 0·0044 A in the conventional conditions of the air — acetylene flame is 0·2 p.p.m. Like the other alkaline earths strontium is not completely dissociated in this flame; the bulk of strontium is present in the form of its oxide. At the temparture of the air — acetylene flame about 11% of the total of strontium are free atoms[1]. The incompleteness of dissociation of the oxide interferes with the determination of strontium by the formation of only slightly volatile compounds. These compounds are formed in the presence of aluminium, titanium, silicates, phosphates, sulphates and some other cations and anions. This interfering effect of the condensed phase is common to all alkaline earthes and has been the subject of many papers; an excellent review has been published by Dean and Rains[2]. In analysis of a geological material the strongest interfering effect is exhibited by aluminium and titanium, whose oxides, in the flame, form compounds with strontium oxide, probably of the spinel type[3]. Another interfering effect in the determination of strontium is its ionization; owing to the low ionization potential part of the strontium atoms are ionized even at the relatively low temperature of the air-acetylene flame[4,5].

To obliterate the interference by aluminium we employed the releasing effect of lanthanum compounds, added in a high excess (1% concentration in the measured solution). A similar procedure was used[6-10] for the other materials. The method of additions[11] is more tedious and not quite reliable.

Strontium can be determined with a higher sensitivity in the acetylene — nitrous oxide flame (0·06 p.p.m., ref.[5]). In this case the interference by the condensed phase is practically eliminated, but the ionization equilibrium must be checked since at the temperature of this flame up to 80% of the strontium ions are ionized[5] and the use of nitrousoxide implies other drawbacks (possibility of back flame, difficulties in obtaining the equipment). For practical use this method has not been recommended.

EXPERIMENTAL AND RESULTS

Apparatus and Chemicals

The measurements were carried out with a Perkin - Elmer spectrophotometer (U.S.A.), Model 303, using a hollow cathode lamp (Hilger and Watts, Great Britain) filled with argon. The chemicals were of analytical grade purity and were checked for the presence of strontium. The purity of hydrochloric acid was of the grade required for semiconductors. Standard solutions of strontium were prepared from strontium carbonate (Johnson and Matthey, Great Britain).

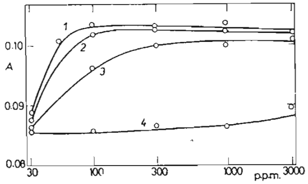

FIG. 1

The Interfering Effect of Ionization on the Determination of Strontium

Concentration of Sr was 4 p.p.m. in dilute hydrochloric acid. Ionization energies (eV): Sr 5·69; K 4·34; Na 5·14; Ba 5·21 Ca 7·72. The curves show the effects of K *1* Na *2*, Ba *3*, Ca *4*.

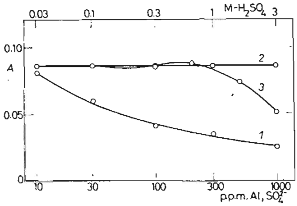

FIG. 2

The Interfering Effect of the Condensed Phase on the Determination of Strontium

Concentration of Sr was 4 p.p.m. The curves show the effects of Al^{3+} *1*, SO_4^{2-} *2*, H_2SO_4 *3*.

The Interfering Effect of Ionization

The ionization equilibrium of strontium is affected by the presence of elements of low ionization energy. The consequential increase in the concentration of free electrons suppresses the ionization of the element to be determined, whose signal is then stronger. We have investigated the effects of the elements whose incidence in the analysed materials is frequent. Fig. 1 shows that these effects are not considerable, since only a small part of strontium atoms are ionized.

The Interfering Effect of the Condensed Phase

The most frequent interfering elements in geological materials are aluminium and titanium. Other interfering cations (Zr, Cr) are usually not present in appreciable quantities. The same is true of sulphate and phosphates (decomposition by sulphuric acid must naturally be avoided). The effects of Al, Ti, Zr and SO_4^{2-} on the signal of strontium are shown in Figs 2 and 3. A considerable negative effect is exhibited by silicates. Silicon dioxide is quantitatively removed from the silicates in the form of SiF_4, evaporated in the course of their decomposition.

To suppress the influence of the condensed phase we tried combining the releasing effect of lanthanum with the effect of an organic reagent (oxine). We had employed a similar procedure previously for the determination of magnesium[12]. The effect of the organic reagent has not yet been clearly explained. By combining the two effects the interference by the condensed phase is more suppressed, though the concentration of lanthanum is only 0·2% instead of the usually employed concentration of 1 to 2%. This reduces the risk of involving impurities into the analysis and the total concentration of salts in the measured solution is decreased, which is another favourable circumstance (the torch does not get choked, the measuring is more stable). The interference by aluminium and titanium can be suppressed up to a concentration of 1000 p.p.m. Al + 500 p.p.m. Ti. In practice this limit is hardly ever reached or exceeded.

In the presence of oxine and an excess of lanthanum ions the interference by ionization is also suppressed (as a result of the rather low ionization energy of lanthanum). Since the other possible interfering effects (*e.g.* a change of the dissociation equilibrium) are reduced as well this simple method is directly applicable to any of the considered materials.

Analytical Procedure

The silicate is decomposed in the usual way (by a mixture of perchloric acid and hydrofluoric acid). After the decomposition the mixture is taken to dryness and the remaining fluorides are removed by the addition of a saturated solution of boric acid (5 ml) followed by evaporation. The residue is dissolved in 20 ml of water and 5 ml of concd. hydrochloric acid, made up to

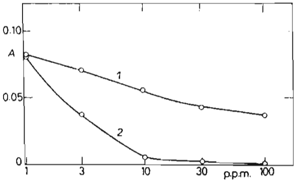

FIG. 3

The Interfering Effect of the Condensed Phase on the Determination of Strontium

Concentration of Sr was 4 p.p.m.; the interfering elements were present in the form of chlorides in dilute HCl. Curves *1* and *2* show the effects of Zr and Ti, respectively.

a volume in a volumetric flask, then transferred into a polyethylene bottle and kept as a stock solution.

TABLE I

Results Obtained by Different Methods (% Sr)

Sample	Calibration curve	Method of standard addition	Method of X-ray fluorescence
Silicate 1	0·017	0·018	—
Silicate 2	0·104	0·098	0·096
Silicate 3	0·14	0·14	0·13
Silicate 4	0·093	0·094	—
Silicate 5	0·060	0·059	0·053
Silicate 6	0·0068	0·0070	—
Silicate 7	0·014	0·0013	0·014
Silicate 8	0·062	0·061	—
Baryte 1	0·88	0·90	—
Baryte 2	0·58	0·57	—
Aragonite	0·27	0·28	—

TABLE II

Analyses of Standard Samples

Sample	% Sr	
	found	recommended value
G - 1[a]	0·027	0·028
T - 1[a]	0·038	0·041
Spilite[b]	0·020	0·022
Granite[b]	0·014	0·013
Limestone[b]	0·056	0·056
Shale[b]	0·017	0·016
Baryte I (Rudňany)	0·88	0·91
Baryte II (Spišská N. Ves)	0·58	0·60
Aragonite (Karlovy Vary)	0·27	0·26

[a] Standards from U.S. Geological Survey, Washington, [b] standards from Zentr. Geol. Inst., Berlin; the other samples are standards of our institute. The standard deviation calculated from 10 results was 0·0007%. The coefficient of variation was 4·85%.

Carbonates and barytes are decomposed by fusion with sodium carbonate. The cold melt is extracted by water, the undissolved carbonate is collected on a filter and dissolved in dilute hydrochloric acid.

To an aliquot portion of the solution to be measured a tenth volume of a standard lanthanum solution (23·45 g of La_2O_3 + 100 g of oxine in 1 liter of azeotropic HCl) is added. The solutions employed to construct a calibration curve (0 to 30 p.p.m.) are prepared by dilution of a standard solution and contain the same portion of the lanthanum solution as the samples to be analysed. The line employed for the determination of strontium was the Sr 4607 Å line. The flame should be moderately reducing. The flow rates of the gases, especially acetylene, must be strictly constant.

Table I gives the results obtained with the aid of a calibration curve in comparison with those obtained by the method of a standard addition and by the method of X-ray fluorescence. Table II gives the results obtained with some standard solutions.

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