Determination of Copper, Zinc, Manganese and Iron in Silicate Samples by Atomic Absorption Spectroscopy

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Reliable methods for the determination of copper, zinc, manganese and iron in silicate rocks are given. Possible interference effects are investigated and precision and accuracy evaluated. All elements are determined directly after decomposing the sample with hydrofluoric and perchloric acids using the spectrophotometer Perkin—Elmer Model 303. The results are reliable for the contents higher than 0.0004% for copper and zinc and 0.001% for manganese and iron in silicate samples, respectively.

Iron and manganese determinations are regular parts of the well-established complete wet-chemical silicate analysis. However, manganese is only in few cases present in sufficient concentration especially in separated minerals so that the ordinary chemical analysis is not reliable enough. In these cases and especially when minute amounts of manganese and also iron are present, the atomic absorption with its simplicity and reliability represents an excellent analytical tool. This is particularly true for the determination of such trace elements as copper and zinc. The detection limits are reasonable being about 0.005 mg/l for Cu and Zn and 0.01 mg/l for manganese and iron (reported for the Perkin—Elmer spectrophotometer Model 303). There were reported minor interference effects for manganese [1, 2] and iron [3] while no interferences were observed for copper and zinc.

Experimental

Apparatus

For all experiments the Perkin—Elmer Model 303 atomic absorption spectrophotometer was used with wide-slot burner; Perkin—Elmer hollow cathode lamps for copper and zinc, ASL lamp for manganese and a Jarrell—Ash lamp for iron were employed. All were neon-filled.

Chemicals

Most chemicals were of the anal. grade from Lachema Brno; hydrochloric and hydrofluoric acids were of „For semiconductors" grade and were checked for the content of iron and zinc.

Standard solutions

Stock solutions for zinc, copper and manganese were prepared by dissolving 1 g of high purity metals in nitric acid and making up the volume to 1000 ml by twice distilled water.
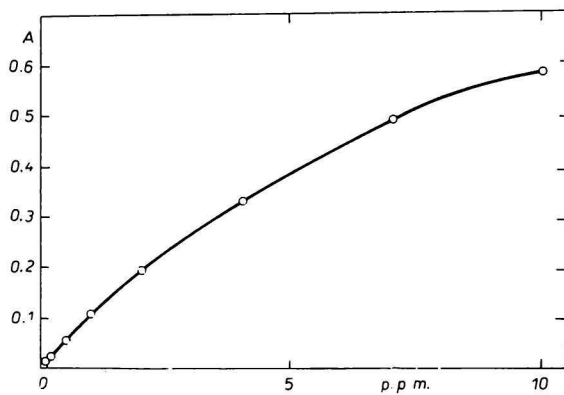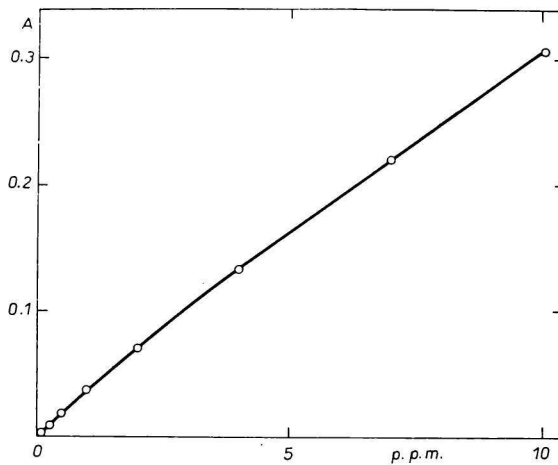
Fig. 1. Analytical curve for zinc.
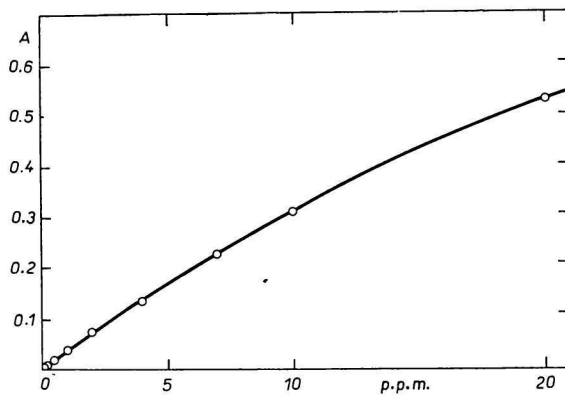

Fig. 2. Analytical curve for copper.

Fig. 3. Analytical curve for manganese.

Stock solution for iron contained also 1000 mg/l of iron and was prepared by dissolving 7.0216 g of Mohr salt $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ in 500 ml twice distilled water; to this solution 25 ml of 6 N hydrochloric acid were added and the volume was made up to 1000 ml.
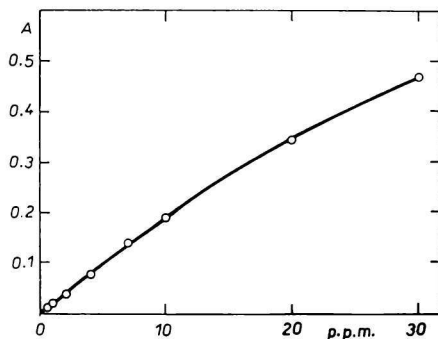

Fig. 4. Analytical curve for iron.

The basic set of standards for construction of analytical curves was prepared from these stock solutions. Mixed solutions with concentrations 0.05—10 mg/l were prepared for copper and zinc (Figs. 1 and 2). The concentration interval was 0.08—30 mg/l for manganese (Fig. 3) and 0.5—30 mg/l for iron, respectively (Fig. 4).

Blank solutions were also prepared for all elements. Standard solutions were prepared in the volume of 100 ml where 5 ml of hydrochloric acid were added; when stored in polyethylene bottles, they are usable for several months.

Interference effects

The interference effects of cations and anions which can be expected to be present in a silicate matrix were investigated. No interference for iron, manganese and copper was found whereas for zinc it is substantial to have less than 2000 mg/l of sodium or
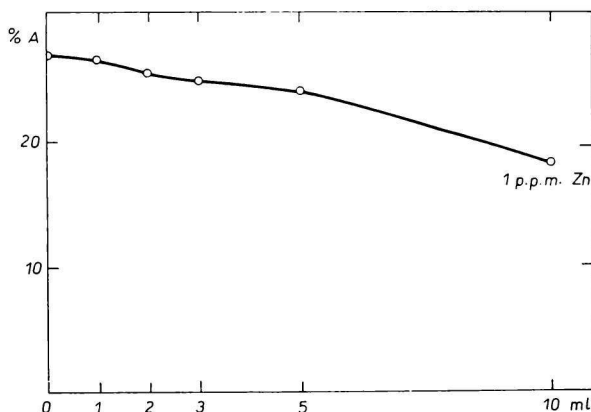

Fig. 5. The influence of sulfuric acid (ml 0.02 N-H_2SO_4) on the determination of zinc.

1000 mg/l of calcium in the solution. Higher concentrations cause serious flame emission which infers stability of measurement even if the stable double-beam spectrophotometer is used. This inconvenient effect can be easily overcome by dilution of the solution measured as the sensitivity of zinc determination is high enough. The influence of silicon was not studied as far as silicon was removed during decomposition of the sample with hydrofluoric acid. Following cations were investigated: Na (1000 mg/l), K (1000 mg/l), Al (3000 mg/l), Ca (3000 mg/l), Fe (1000 mg/l), Ti (1000 mg/l) for 1 mg/l of Zn, 0.5 mg/l of Cu, 0.5 mg/l of Mn and 5 mg/l of Fe. With these concentrations, the interference effects of various acids were also studied, namely those of hydrochloric, nitric and sulfuric acid. The negative influence by the last one on zinc was observed as it is shown in Fig. 5.

With the determination of zinc it is absolutely necessary to maintain highest purity of chemicals, water, chemical glass and overall environment as this element due to its high mobility is practically „omnipresent". Also metal parts of the burner can cause contamination by zinc [4] when strong acid media are used for measurements; this can be improved by coating these parts with some plastic material [5].

Sample treatment

The decomposition of the sample by hydrofluoric and perchloric acid was used. In this way the silicon oxide is removed and all determinations after dilution to suitable concentration are free of interferences.

0.1—1 g of the sample is weighed to platinum or PTFE dish. After some drops of water, 5—10 ml of hydrofluoric acid is added and then 0.5—1 ml of perchloric acid. The sample is heated on the sand bath to the first fumes of perchloric acid. Then another 5 ml of hydrofluoric acid is added and the sample is heated to the fumes once more. After a while of cooling 5 ml of boric acid (sequestration of the fluoride residue) is added and the sample is evaporated gently just to the dryness. 15—20 ml of warm twice--distilled water is added to the dry residue and after 15 minutes of digestion, the whole sample is dissolved by addition of 5 ml of hydrochloric acid. The volume is made up to 100 ml and the solution is transferred to the polyethylene bottles. When the concentrations of elements analysed are not expected to be too high i.e. dilution is not needed, the sample is prepared for measurement. The convenient concentration interval is 0.05—10 mg/l for copper and zinc, 0.1—30 mg/l for manganese and iron (see Fig. 1—4). For all measurements the conditions recommended by manufacturer were maintained, namely the most sensitive lines Zn 213.8 nm, Cu 324.7 nm, Mn 279.5 nm and Fe 248.3 nm, slit widths, fuel and oxidant flow rates, hollow cathode current, etc.

Results

The accuracy of the method was checked comparing the results with standard samples, with results obtained by other analytical methods and also by the standard addition method. Precision was calculated as the standard deviation from two parallel determinations according to the equation

$$S = \sqrt{\frac{\sum_i (x_i - x_i')^2}{M}}$$

when x_i and x_i' are two results of one sample and M is the total of analyses.

Table 1

The accuracy of the determination of copper
(Results in per cent)

Sample	Atomic absorption	X-ray fluorescence	Recommended value
Granite G-1	0.0013	—	0.0011
Diabase W-1	0.0117	—	0.0110
Claystone	0.0012	0.0012	—
Porfyre	0.0104	0.0098	—
Shale ZGI	0.0056	—	0.0060
Granite ZGI	0.0018	—	0.0014
Spilite ZGI	0.0048	—	0.0048

Table 2

The accuracy of the determination of zinc
(Results in per cent)

Sample	Atomic absorption	X-ray fluorescence	Recommended value
Granite G-1	0.0059	—	0.0055
Diabase W-1	0.0116	—	0.0110
Siliceous sandstone	0.0062	0.0067	—
Siliceous sandstone	0.0067	0.0070	—
Siliceous sandstone	0.0046	0.0053	—
Claystone	0.0049	0.0048	—
Porfyre	0.0052	0.0048	—
Porfyre	0.0023	0.0020	—

Table 3

The accuracy of the determination of manganese
(Results in per cent)

Sample	Atomic absorption	Chemical determination	Recommended value
Claystone	0.051	0.047	—
Tuffite	0.13_6	0.12_4	—
Basalt	0.14_5	0.13_2	—
Spilite	0.19_5	0.13_2	—
Syenite	0.074_8	0.070	—
Ferrite	0.021_1	0.21_6	—
Ferrite	0.020_4	0.20_1	—
Shale ZGI	0.050	—	0.050
Granite ZGI	0.044_4	—	0.040
Spilite ZGI	0.14_5	—	0.14_5
Granite G-1	0.029_1	—	0.026—0.030
Diabase W-1	0.18_4	—	0.16 —0.18

Table 4

The accuracy of the determination of iron
(Results in per cent)

Sample	Atomic absorption	Chemical determination	Recommended value
Granite G-1	2.04	—	2.04
Diabase W-1	11.28	—	11.22
Glass sand	0.037	0.037^b	
		0.037^c	—
Syenite	0.65	0.70^a	—
Syenite	0.80	0.80^a	—
Syenite	0.36	0.40^a	—
Ferrite	4.85	4.80^a	—
Ferrite	3.21	3.21^a	—
Ferrite	0.86	0.90^a	—
Ferrite	0.46	0.50^a	—
Serpentinite	3.46	3.31^a	—
Shale ZGI	6.93	—	6.90
Granite ZGI	2.03	—	2.0
Spilite ZGI	9.69	—	9.6

a) Bichromate titration; decomposition with Na_2CO_3 fusion.
b) Spectrophotometry with α,α'-dipyridyle; decomposition $HF + HClO_4$.
c) Spectrophotometry with *o*-phenantroline; decomposition $HF + HClO_4$.

The standard deviation calculated for iron from 2 parallel determinations including decomposition is 1.51% rel., for zinc from 30 parallel determinations 4.66% rel., for manganese from 20 parallel determinations 4.26% rel., and for copper from 28 parallel determinations 4.10% rel., respectively. The illustration of the accuracy is given in Tables 1—4.

The smallest concentration which can be determined with this precision (when weighing 1 g of the sample to the volume of 50 mg/l) is 0.0004 per cent, 0.0004 per cent, 0.0005 per cent and 0.001 per cent for copper, zinc, manganese and iron, respectively.

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