

## DETERMINATION OF Zn, Mn AND Fe IN SOME MINERALS BY FLAME ATOMIC ABSORPTION SPECTROMETRY

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**Abstract:** A rapid and simple method for the determination of iron, manganese and zinc in some sulfide (galena and sphalerite), carbonate (siderite, aragonite) and sulfate (gypsum) minerals is based on atomic absorption spectrometry. The samples were dissolved in a mixture of  $\text{HNO}_3$  and  $\text{HCl}$ . The effects of interfering elements (Pb, Zn, Ca and Fe) on the determination of Fe, Mn and Zn in the investigated minerals were studied. These investigations show that it is possible to determine iron, manganese and zinc directly from solutions obtained by dissolution of minerals in mineral acids ( $\text{HCl}$  and  $\text{HNO}_3$ ), except in the case of determination of manganese in calcium matrices. It was found that the presence of calcium tends to decrease the absorbance of manganese. Procedures were verified by the method of standard additions and results were compared with those obtained by inductively coupled plasma-atomic emission spectrometry (ICP-AES). It was also found that the detection limit for all investigated elements in minerals is  $2 \mu\text{g g}^{-1}$  for Zn and  $5 \mu\text{g g}^{-1}$  for Mn and Fe. The investigated minerals originates from different mines from the Republic of Macedonia.

**Key words:** Iron, manganese, zinc, atomic absorption spectrometry, sphalerite, galena, siderite, aragonite, gypsum

### 1. Introduction

The principal advantage of flameless atomic absorption spectrometry, i.e., the detection limits, which are extremely low in comparison with other methods and are attainable for a great number of elements, makes this technique particularly suitable for the determination of elements present in geochemical materials in concentration of the order of ppb. Iron, manganese and zinc are of great interest in geochemistry for a better understanding and interpretation of various geological processes. There are a number of investigations concerning the determination of elements investigated in similar geological samples by flame atomic absorption spectrometry (FAAS) and electrothermal atomic absorption spectrometry (ETAAS). Some authors have investigated the possibility of the determination of these elements directly from the sample solution, by flame AAS [1-7], or by ETAAS [7]. The influence of interfering elements was of particular interest: in the flame AAS determination [8-10], or in the ETAAS determination [11]. In this work we propose a method for directly determination of Zn, Mn and Fe with atomic absorption spectrometry from the solution obtained by a dissolution of investigated minerals in mineral acids.

### 2. Experimental

#### 2.1. Instrumentation

A Perkin-Elmer 303 atomic absorption spectrophotometer was used. Light sources were iron, manganese and zinc hollow cathode lamps. The instrumental parameters for the determination of Fe, Mn and Zn are given in Table I.

Table I. Instrumental parameters for determination of Zn, Mn and Fe by flame AAS

Parameters	Zn	Mn	Fe
Wavelength, nm	213.9	279.5	248.3
Slit, nm	1	0.2	0.2
Lamp current, mA	15	10	20
Gas mixture	Acetylene/air		

## 2.2. Procedures

**Sphalerite.** 0.1 to 0.5 g of powdered sample of sphalerite was dissolved in 15 cm<sup>3</sup> of 2 mol dm<sup>-3</sup> HNO<sub>3</sub>. The solution was evaporated to dryness and the residue was dissolved in 5 cm<sup>3</sup> of 2 mol dm<sup>-3</sup> HNO<sub>3</sub>. The solution was transferred to a volumetric flask of 50 cm<sup>3</sup>.

**Galena.** 0.1 to 0.5 g of powdered sample of galena was dissolved in 10 cm<sup>3</sup> conc. HNO<sub>3</sub> and 2 cm<sup>3</sup> of H<sub>2</sub>O<sub>2</sub>. The solution was evaporated to dryness, the residue was dissolved in 2 cm<sup>3</sup> HNO<sub>3</sub> and 10 cm<sup>3</sup> of 2 mol dm<sup>-3</sup> HNO<sub>3</sub> and the solution was transferred into a volumetric flask of 50 cm<sup>3</sup>.

**Siderite, aragonite, gypsum.** 0.1 to 0.5 g of a powdered mineral sample was dissolved in 5 cm<sup>3</sup> of conc. HCl and 1 cm<sup>3</sup> of conc. HNO<sub>3</sub>. A few drops of H<sub>2</sub>O<sub>2</sub> were added and the solution evaporated to near dryness. The residue was dissolved in 2 cm<sup>3</sup> of concentrated HCl and the solution was transferred into a volumetric flask of 50 cm<sup>3</sup>.

## 3. Results and Discussion

Because it is sensitive and specific, atomic absorption spectrometry (AAS) is widely used in geochemical analysis. For sample dissolution usually an acid digestion is used. However, acid digestion produces solutions that contain different ions of elements dissolved from the sample matrix, which may interfere with the determination of iron, manganese and zinc. The interference of Pb, Zn, Ca and Fe as matrix elements was studied. Series of solutions with the same concentration of Fe, Mn and Zn and various concentrations of interfering elements were prepared, so that the concentrations of these elements were similar to the concentrations in the sample solutions. Results from these investigations are given on Figs. 1-4. As it can be seen, Fe, Mn and Zn can be determined in galena (Fig. 1), Fe in Ca-minerals (Fig. 2), Fe and Mn in sphalerite (Fig. 3) and Zn in siderite (Fig. 4) when 0.5 g of mass is used. Zn in Ca-minerals (Fig. 2) and in siderite (Fig. 4) can be directly determined when 0.25 g is used.

Using the proposed methods, some samples of the investigated minerals (with and without standard additions) were dissolved and Fe, Mn and Zn were determined. Results show satisfactory recovery values. These results are compared with those obtained by ICP-AES and similar results were obtained. The content of Fe in investigated minerals ranges from 10 to 500 µg g<sup>-1</sup>; of Zn is below limit of detection in Ca-minerals, from 1 to 100 µg g<sup>-1</sup> in galena; of Mn ranges from 1 to 50 µg g<sup>-1</sup> in galena and gypsum and from 1 to 250 mg g<sup>-1</sup> in sphalerite and siderite. The detection limit of the method was found to be 2 µg g<sup>-1</sup> for Zn and 5 µg g<sup>-1</sup> for Mn and Fe.

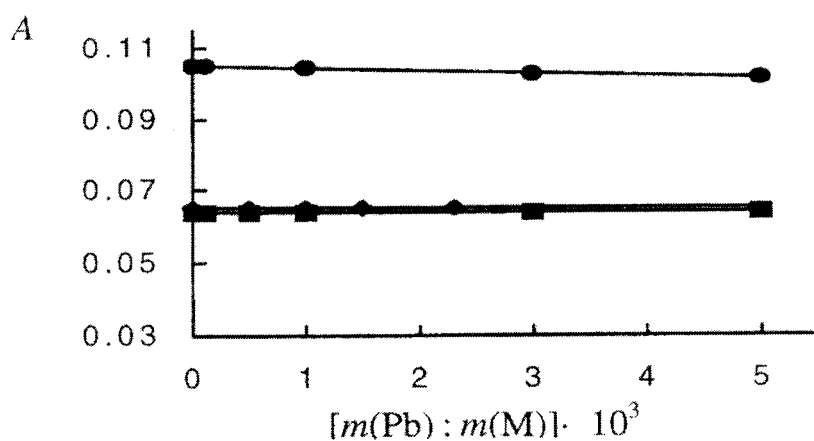


Fig. 1. Influence of Pb as a matrix element on Fe (♦), Mn (■) and Zn (●) absorbance

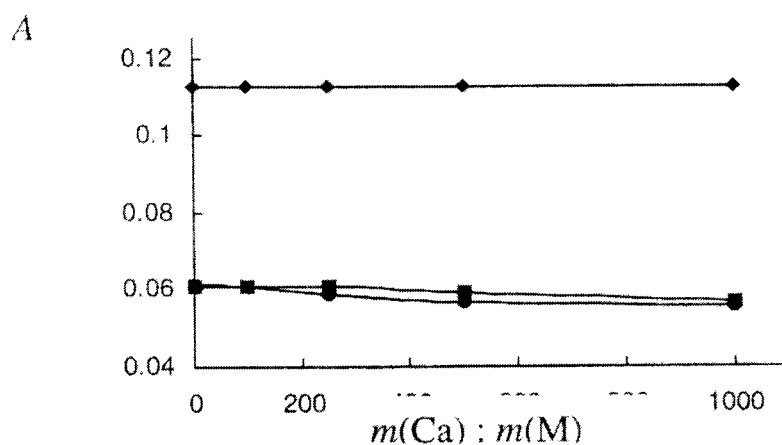


Fig. 2. Influence of Ca as a matrix element on Fe (■), Zn (♦) and Mn (●) absorbance

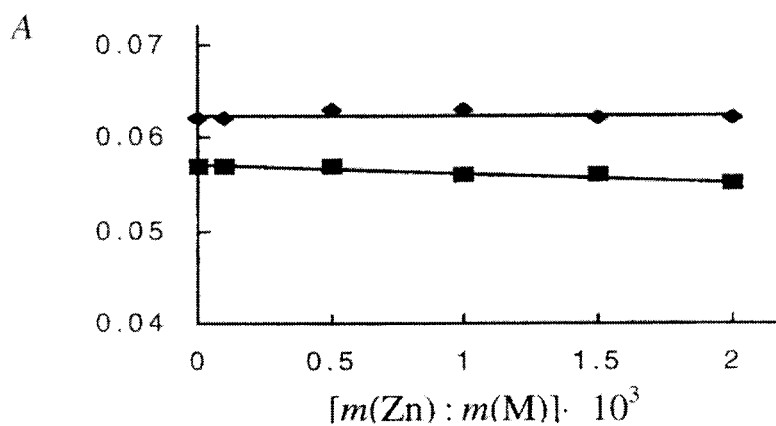


Fig. 3. Influence of Zn as a matrix element on Fe (♦) and Mn (■) absorbance

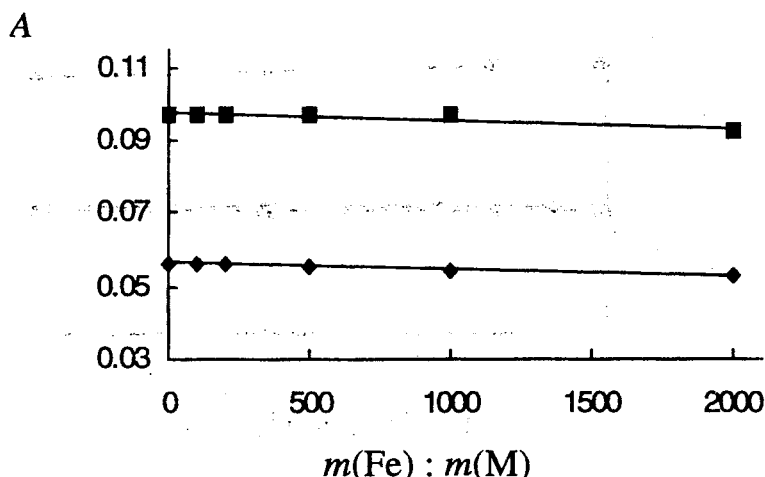


Fig. 4. Influence of Fe as a matrix element on Mn (◆) and Zn (■) absorbance

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**Апстракт.** Предложена е метода за определување на Fe, Mn и Zn со пламена атомска апсорпциона спектрометрија во различни сулфидни (галенит и сфалерит), карбонатни (сидерит, арагонит) и сулфатни (гипс) минерали. Испитувањето на влијанијата на матрицата покажа дека е можно директно определување на Fe, Mn и Zn од раствори добиени со растварање на минералите во смеси од киселини (HCl и HNO<sub>3</sub>), освен во случајот на определувањето на Mn во калциумови матрици. Утврдено е дека присуството на калциумот доведува до намалување на апсорбанцата на Mn. Постапките се потврдени со методот на стандарден додаток и со споредба на резултатите со оние добиени со примена на атомската емисиона спектрометрија со индуктивно спрегната плазма. Утврдено е дека границата на детекција изнесува 2  $\mu\text{g g}^{-1}$  за Zn а 5  $\mu\text{g g}^{-1}$  за Mn и Fe. Испитуваните минерали потекнуваат од различни рудници од Република Македонија.