INDIRECT DETERMINATION OF SULPHUR DIOXIDE AND SULPHURIC ACID BY FLAME ATOMIC ABSORPTION SPECTROMETRY

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ABSTRACT. We have developed a new technique based on the rules of high-temperature processes in flame for the indirect determination of sulphur dioxid, sulphuric acid and phosphoric acid in natural samples by flame atomic absorption spectrometry (FAAS). The main point of the method is the difference in atomizaton of various inorganic salts of magnesium based on their thermal differences. In particular the magnesium perchlorate gives 10 times greater absorbance signal than the magnesium sulphate in the same concentration. The absorption of sulphur dioxide from air in hydrogen peroxide gives sulphuric acid, which can be determined by the previously mentioned method. The detection limit of the new method for sulphuric acid is $1.5 \cdot 10^{-6}$ mol/L while the range of determination for is $3 \cdot 10^{-6} – 4.1 \cdot 10^{-5}$ mol/L. Since FAAS is one of the fastest analytical methods, our indirect FAAS acid determination is capable for serial analysis. With this new method we have determined the sulphuric acid content of the atmosphere of a battery recharging facility.

Keywords: sulphur dioxid, sulphuric acid, atomic absorption, acid determination

INTRODUCTION

Sulphur is of great importance in the environment. It can be found in forms of organic, inorganic and biologically vital compounds in the nature. The antropogenic activity have had a great influence on the biogeochemical cycle of sulphur in the past decades. Sulphur dioxid is one of the most important pollutants of air. Although in the last 40 years the sulphur content of air of big cities has decreased significantly, in developing countries it is still a major air pollutant. It exerts it's harmful effect in form of gas and by the combination with aerosols and smoke. In the presence of moisture and in oxidizing environment it changes to sulphuric acid, which is one component of acid rain. On the other hand sulphur containing organic substances are building stones of living organisms. For the determination of certain sulphur containing compounds several classical analytical methods have been used recently, which are often complicated and require long lasting laboratory work. These resulted the spreading of fast instrumental analytical methods capable for serial analysis. One of the most often used methods for the determination of sulphur dioxid concentration from air is the West-Gaeke method which is based on a complex formation and it's spectrophotometric determination (Radojević et al., 1999). Recently apparatuses are available on the market, which are highly sensitive, selective and indicates direct concentrations, although in some countries e.g. in the USA the West-Gaeke method is still the reference method.

For the determination of sulphates in water and in solutions generally barium chloride is used to form the barium sulphate precipitation, which is detected by turbidimetry or gravimetry. Recently for the determination of sulphate ionchromatography has been used as well. Most of the previously described methods are patented, strict steps must be kept and they are often complicated and requires special reagents, thus they are incapable for serial analysis.

MATERIALS AND METHODS

All chemicals used were of analytical grade. The standard solutions used for calibration were manufactured by Merck and Spectrascan, and we used acids from Carlo Elba and Sharlau. The solutions were prepared with ion exchanged water, the magnesium salts were prepared from magnesium oxide (Merck) by the dissolution of oxides in the proper acid. For the atomic absorption measurements Unicam SP1900 flame atomic absorption spectrometer and multislot burner with oxidizing air/acetylenee flame were used. For the weight measurements we used Precisa 240A analytical balance. All dilutions were carried out with Biohit mechanical pipettes. The potenciometric titration was carried out by Thermo Electron Corporation ORION 2 STAR pH Benchtop pH meter equipped with Radiometer Copenhagen AUTOBURETTE ABU 13 automatic burette.

Determination of acids and anions in trace amounts with FAAS

A common property of indirect methods that we can determine the desired component with FAAS, but we can detect an other species, which takes part in a reaction in which it reacts with the target component with well defined coefficient. These methods can be

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divided into two groups. In the first group we can find methods which are based on precipitation (Rose et al., 1969; Smith et al., 1972), complex formation (Jungreis et al., 1976; Jones et al., 1976) , redoxy reactions (Oles et al, 1974) and determination of excess metals. The other group contains methods which are based on reactions undergoing in the atomizing unit, resulting the change of absorption signal depended on the properties of ligands/anions.

Methods in the second group are relatively fast and requires simpler sample preparation (Bond et al, 1968). The atomic absorption inhibition titration(AAIT) first used by Looyenga and Huber (Looyenga et al., 1971) is especially remarkable, in which they utilized the signal decreasing effect of sulphates, phosphates, silicates and fluorides on the absorbance of alkali earth metals (Lin et al, 1972). Although the fact that each sample requires a new titration makes a hindrance to serial analysis. In this work we have developed a new

method for the indirect FAAS determination of some acids and anions, which is relatively cheap, fast, reliable and capable for serial analysis.

Theoretical bases of the new method

From analytical view the atomizing unit functions properly if the number of ground state atoms formed and the absorption signal directly proportional to it depend only upon the sample concentration , however it is independent from the matrix of the desired element.

Magnesium salts in reducing acetylene/air flame optimal for alcali erth metals show very similar, anion independent atomic distribution in flame (fig 1A), while under inordinate circumstances (special burner, highly oxidizing acetylene/air flame, extremely low observation height) absorption signals of salts with different anions significantly differ from each other (1B).
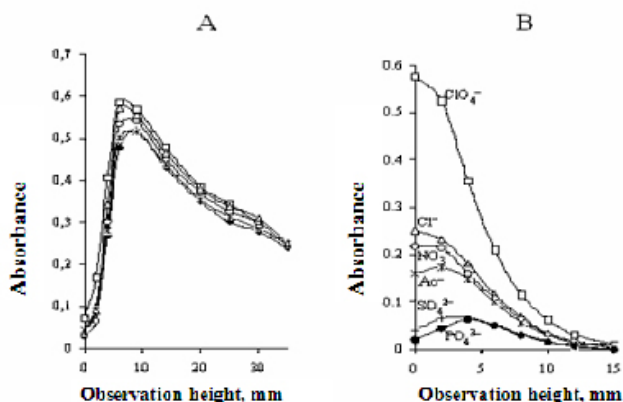

Fig. 1 Atomic distribution of magnesium salts with different anions in conventional one slot burner with reductive air/acetylene flame (A) and in multislot burner with highly oxidizing air/acetylene flame (B). The concentration of magnesium salt is in each sample 1 mg/L
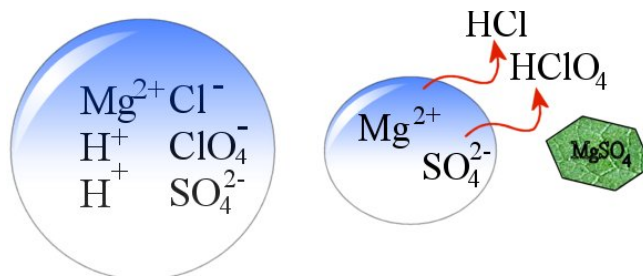

Fig. 2 Formation of dry aerosol from a salt solution containing different acids

These phenomena can be used for the studying of mechanisms of atomizition processes and for the indirect FAAS determination of anions.

After the liquid aerosol enters the flame, it overgoes through several physical and chemical transmutation until it decomposed into ground state elements. The

first step is the evaporation of the solvent to give dry aerosol. This process is of vital importance for the subsequent atomization steps, because the physical and chemical composition and thermal properties of the dry aerosol determine the direction and rate of the further processes (solid phase reactions, thermal

decomposition, melting, evaporating, sublimation, dissociation etc.). We investigated what happens when a sample contains more than one anion simultaneously, what will be the composition of the dry aerosol. For this purpose we titrated the given salt with different acids by the help of a continuous AAS titration device. By this way we can follow directly the absorption change in flame as a function of acid concentration. As a result we concluded the given metal ion will form solid aerosol from the mixture of anions which are present at least in stoichiometric ratio with the less volatile one(Fig 2.). This means in the drying process

of the aerosol, from a solution containing two or more acids first the most volatile ones will be expelled leaving back the less volatile one which will take part in the formation of solid salt. These results the creation of a salt forming order of anions which is independent from the metal and it is valid in general for anions.

This anion sequence is the following:

$$CH_3COO^- \rightarrow Cl^- \rightarrow NO_3^- \rightarrow Br^- \rightarrow I^- \rightarrow ClO_4^- \rightarrow SO_4^{2-} \rightarrow PO_4^{3-}$$
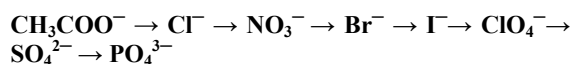
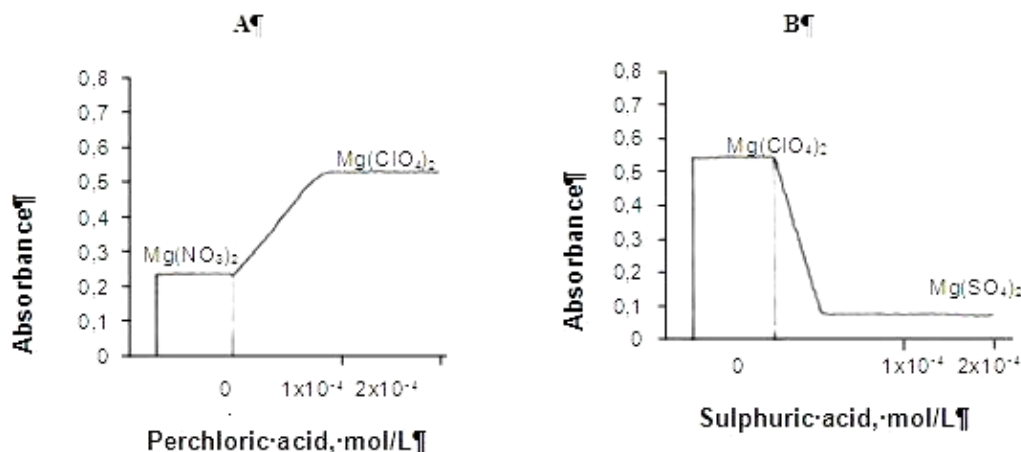This order was given the name salt forming order.

Fig. 3 The titration curve of magnesium nitrate with perchloric acid (A) and the titration curve of magnesium perchlorate with sulphuric acid (B) at low detection hight in oxidazing acetylene/air flame
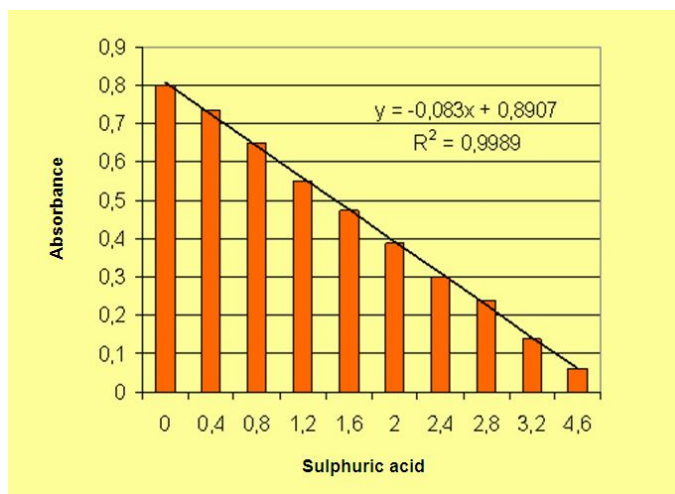

Fig. 4 Calibrating series for sulphuric acid determination

As we could see in figure 1 the different salts of alkali metal ions give different absorption signal especially at low observation hight of a rather low temperature flame. If we take the absorption of acetate, chloride and nitrate as an average signal, the absorption signal of magnesium perchlorate is 2-3

times grater and the signal of nitrate and phosphate is one tenth of perchlorate. This inordinate behavior of alkali earth metal salts and the salt forming order have made us possible to develope a rapid and for serial analysis capable atomic absorption method.

On the basis of the two titration curve shown in figure 3. the principle of the method is the following: if we add perchloric acid to magnesium nitrate or acetate (which are at the begining of the salt forming order) the absorbance signal increases linearly until we reach a perchlorate concentration, which is stoichiometric to the magnesium concentration. We used 1 mg/L Mg salt which is equal to 4×10^{-5} mol/L perchloric acid.

These linear changes make us possible to prepare such calibrating solutions shown in Fig 4, which contain beside the magnesium salt sulphuric acid in varying concentration.

RESULTS AND DISCUSSION

Determination of sulphur dioxide from air

In our method we determined the sulphur dioxide in air by absorbing it in hydrogene peroxide to give sulphuric acid. The formed sulphuric acid can be determined by the previously mentioned atomic absorptoin method for magnesium. Although we can determine the sulphur dioxid content of air precisely only if we know the efficiency of absorption. For this purpose we liberated known amount of sulphur dioxide from the following reaction:

$$Na_2SO_3 + 2HCl = 2NaCl + SO_2 + H_2O \qquad (1)$$

The sulphur dioxide was absorbed in 1, 5, 10, 30 m/m% hydrogene peroxide respectively. In the absorption process sulphur dioxide is converted into sulphuric acid as follows:

$$SO_2 + H_2O_2 = H_2SO_4 \qquad (2)$$

From the results we concluded that the efficiency of the absorption increases with the concentration of hydrogene peroxide. However as you can see in table 1 there are only slight difference between 10% and 30% hydrogene peroxide, thus respect to the highly oxidizing properties of concentrated hydrogen peroxide which is harmful to the instruments, we found the 10 % concentration as an optimal concentration.

The experimental arrangement of the system is shown in fig. 5.

As we can see in Fig. 5 the eliberated sulphur dioxide is expelled from the solution with nitrogen gas. In order for the complete absorption we lead the sulphur dioxide through 3 sequental impinger containing the hydrogene peroxide. The nitrogen flow was 4 mL/min, the time of absorption was 15 min. Each impinger contained 10 ml of hydrogene peroxide.

Table 1
Absorption efficiency of sulphur dioxide

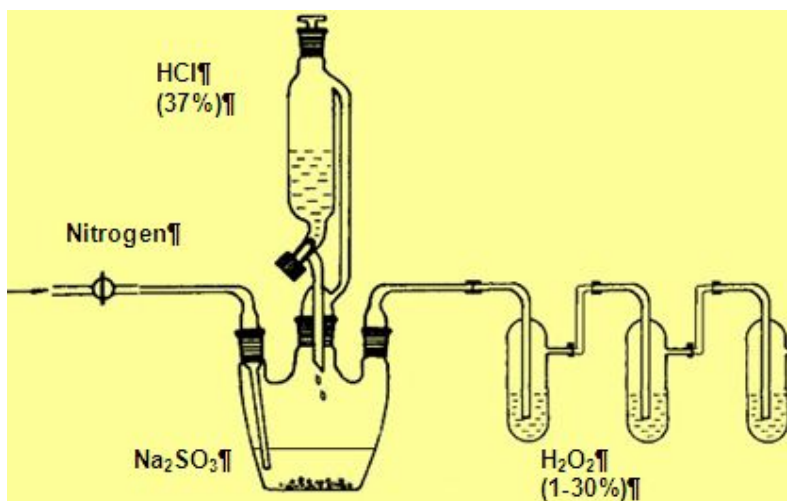| H_2O_2 concentration (m/m%)	Absorption efficiency (%)
1	80.9 %
5	88.3 %
10	92.8 %
30	95.9 %

Fig. 5. Experimental arrangement of the absorption system

Parameters of sulphur dioxide determination

After the absorption of sulphur dioxide the excess hydrogene peroxide was removed by boiling. From this solution we added 200 μL to a 1 mg/L Mg(ClO$_4$)$_2$ solution. The atomic absorption parameters used for samples and calibrating solutions are summerized in Table 2.

The detection limit for sulphuric acid 0.15mg/L ($1.5 \cdot 10^{-6}$ mol/dm^3) The range of determination of the method, for sulphuric acid 0.3-4 mg/L.

Determination of sulphuric acid from the atmosphere of a battery recharging facility

Since in the process of battery recharging sulphuric acid can pollute the air, it was obvious to test our methode there. The air samples were taken with 10 mL volume impingers. It contained distilled water as absorbing agent. The air was sucked through the impinger by the rate of 60 L/min for 50 minutes thus a sample contained the sulphuric acid content of 50 L air. To follow the efficiency of the absorption we used 3 series-connected impinger. The sampling were carried out at a height of 150 cm at five different locations of the facility. In order to get an overall picture from the pollution of the air, the sampling was carried out throught 2 shift. The results are shown in table 3.

As we can see from the results, the values never exceeded the maximum allowed concentration (1000 $\mu g/m^3$).

Table 2

Atomic absorption parameters of sulphur dioxide determination by FAAS

Flame	Acetylene/air
Acetylene flow	0,56 L/min
Air flow	4,5 L/min (3 bar)
Burner	Multislot
Observation hight	2 mm
Nebulising velocity	4,0 mL/min
Wavelength	285.2 nm
Slit	0,15 mm
Mg^{2+} concentration	1 µg/mL

Table 3

The sulphuric acid content of air in a battery recharging facility

Sample number	1	2	3	4	5	6	7	8	9	10
Start of sampling (hour)	9.40	10.50	12.00	13.10	14.20	15.30	16.40	17.50	19.00	20.10
End of sampling (hour)	10.30	11.40	12.50	14.00	15.10	16.20	17.30	18.40	19.50	21.00
Sampling location	1	2	3	4	5	1	2	3	4	5
Conc. of H_2SO_4 ($\mu g/m^3$)	210	380	286	456	598	572	290	380	364	364
[H_2SO_4]/ MAC[*]	0.21	0.38	0.29	0.46	0.60	0.57	0.29	0.38	0.36	0.36

[*]MAC (Maximum allowable concentration) = 1000 $\mu g/m^3$

CONCLUSIONS

We can conclude that we developed a new analytical method for the indirect FAAS determination of sulphuric acid which is rapid, relatively cheap and capable for serial analysis.

ACKNOWLEDGMENTS

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