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A LABORATORY POLAROGRAPHIC RECORDER FOR SULFUR DIOXIDE

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A polarographic analyzer was assembled by connecting a polarograph to a simple gas absorption device, using a constant flow of an electrolyte; limiting current for sulfur dioxide in the medium of $0.1N-H_2SO_4$ was recorded. Important factors for the application of the apparatus were determined, such as the influence of the rate of flow of the electrolyte, and the influence of SO_3.

Introduction, and Analysis of the Problem

In 1954, J. Srbek was studying the problem of the use of sulfur dioxide from waste gases in the Research Institute for Inorganic Chemistry. (Results of this work are published on page 137 of this issue.). In laboratory absorption experiments it was necessary to follow continuously the concentration of sulfur dioxide, before and after absorption[1], while operating with a suspension of Zn sulfite and calcined magnesite. The absorption experiments were conducted with an inlet concentration of 0.3-0.4 percent SO_2; the outlet concentration was within the limits of 0.03-0.1 percent.

Several kinds of continous recorders for SO_2 are described in literature. In the majority of sulfuric acid contact plants SO_2 is recorded in continous analyzers of the Kent or Siemens type; SO_2 is determined on the basis of thermal conductivity[2,3]. Abrams' SO_2 analyzer[4], working on the principle of Reich's method[5] is used for the determination of the SO_2 concentration in stack gases in contact plants. The analyzer for the determination of of SO_2 in the presence of SO_3 designed by V. Lakota[6] is based on the reaction:

$$K_2Cr_2O_7 + 3\,SO_2 + 2\,H_2SO_4 = 2\,KHSO_4 + Cr_2(SO_4)_3 + H_2O$$

The resulting Cr salts change from the original orange color to green, and the intensity of this is measured by a colorimeter of a trough flow type.

There are very few published studies dealing with the use of polarography for continous gas analysis. Most authors were concerned with the determination of oxygen in water and in gases[7,8,9,10,11,12]. Measuring of SO_2 concentrations in wetting liquids was studied by L.D. Wilson and R.J. Smith[13].

I selected the polarographic method for the determination of small amounts of SO_2 in the gases leaving the absorption experiments. In my work I used mainly the experience gathered by J.V.A. Novak, laureate of the Klement Gottwald State Prize[4], who was the first to use polarography for long term production measurements, and for the purpose of automation.

Sulfites, in an acid medium, give a cathodic wave, corresponding to the reduction of SO_2 according to the equation

$$SO_2 + 2H^+ + 2\,e = H_2SO_2 \text{ (sulfoxylic acid)}^{[15]}$$

When a constant voltage corresponding to the limiting current for SO_2 is maintained on the electrodes, the increase or decrease in concentration is shown by the increase or decrease of the current. This is the principle of a polarographic analyzer.

During a direct polarographic determination of SO_2 in, for instance, 0.1 N H_2SO_4 it is not necessary to remove atmospheric oxygen from the solution (See Fig 1.). This contributes substantially to the simplification of the apparatus.

Experimental Part and Results

1. Apparatus and the Arrangement Scheme

For the assembly of the apparatus I used the following assumptions:

a) The basic electrolyte used for the absorption of SO_2 must flow through the apparatus at a constant rate

b) SO_2 must be always absorbed in the same volume of electrolyte in the vessel, located in front of the electrolytic vessel, to avoid interference with the measurements.

c) The absorbate and the Hg from the electrodes must flow through the electrolytic vessel at a constant rate.

d) The limiting current must be registered as a function of time.

Figure 1. The Height of the Cathodic Wave of SO_2 as a Function of the Concentration of Sulfur Dioxide

Basic electrolyte: 2.10^{-1} M-H_2SO_4; concentration of SO_2
(1) $4.\ 10^{-2}$; (2) 2.10^{-2} M; (3) 1.10^{-3} M;
(4) 5.10^{-3} M; (5) 0.0 M. Cathode from 0 V without removing of atmospheric oxygen from the solution; SKE; 200 mV/abs; accuracy 1 : 100

The instrument used for the adjusting of the current, and for the recording of the limiting current was a polarograph V 301 arranged so, that when the motor was connected the wheel with the potentiometric wire was not turning, and only the polarographic paper in the recording chamber was moving. Without this modification it would be possible to record on a polarographic paper only measurements lasting 10 minutes. I introduced therefore between the motor and the recording chamber a system of wheels, with a changeable sprocket (Fig 2) so that one polarographic paper can register about 2, 4, and 8 hour long measurements.

The apparatus for the absorption of the tested gas and the scheme of the connection are shown in Figure 3.

A 5-liter bottle Z supplies spare 0.1N H_2SO_4 to a flow regulator B, which maintains a constant rate[2] of flow by the overflow height. The rate of flow of 0.1N H_2SO_4 is regulated by a valve T_1. The electrolyte leaves the inlet regulator, to pass into the absorption vessel A, into which the analysed gas is introduced through a sintered glass plate D under constant pressure, regulated by the height of water column in the cylinder H. From there, the absorbate overflows into the through-flow electrolytic vessel N. The indicating electrode is a mercury drop electrode K_1, with a reservoir height of 50 cm and a time interval of one second for one mercury drop.

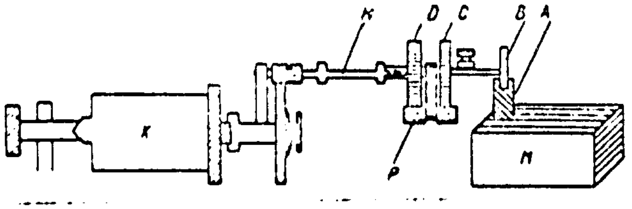

Figure 2. Arrangement of the Polarograph for Recording Lasting Several Hours

A - Screw; B - Screw driving wheel (44 cogs)
P - Driving wheel (14 cogs), H - Connecting shaft,
C - Front stationary wheel (40 cogs).
D - Front interchangeable wheel, rotating; for 2 hours recording 45 cogs; for 4 hour recording 43 cogs, for 8 hours 42 cogs.
K - Recording chamber with photographic paper;
M - Electric motor

As a reference electrode originally a platinum foil was used. It was however found, that after a longer operation, when the electrode is immersed directly in the analyzed solution, it becomes polarized, and lower values for the limit current are registered. Therefore the anode K_2 was a mercury drop electrode[14] with a reservoir height of 70 cm and the rate of one drop of 2.8 secs.

2. The Influence of the Flow Rate of the Electrolyte, SO_3, and Temperature on the Determined Values

These influences were investigated in a synthetic mixture of gases SO_2 and air, that passed through orifices, and the concentration of the SO_2 was regulated by the pressures in the respective flow recorders. During the determination of the influence of the flow rate of electrolyte on the intensity of the limiting current, the pressures of the gases were adjusted so that a galvonometer with an accuracy of 1/100 showed a deviation of 50 mm. When this constant SO_2 concentration was maintained, it was analyzed iodometrically by Reich's method[5] at 0.94 percent SO_2, the flow rates of the 0.1 N-H_2SO_4 were varied, and the height of the limiting current are shown graphically in Figure 4.

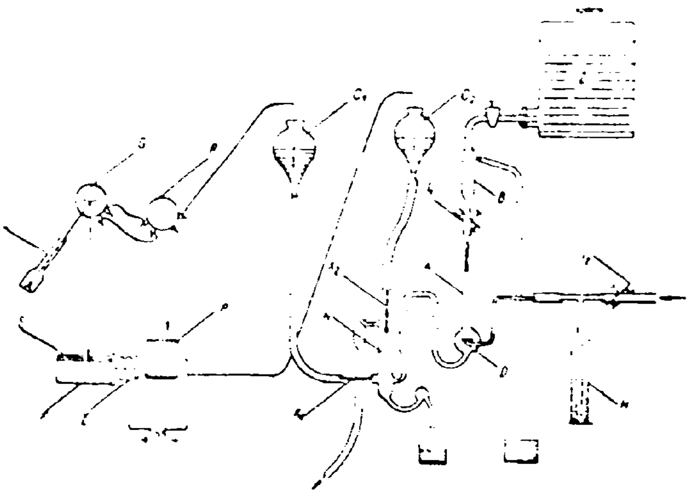

Figure 3. Apparatus for Absorption of the Analyzed Gas, and the Schematic Connections of the Equipment

Z - bottle with stored 0.1 N-H_2SO_4 solution
B - flow regulator T_1, T_2 - regulating valves
A - absorption vessel   N - through flow electrolytic cell
K_1, K_2 - mercury drop electrodes C_1, C_2 - reservoirs
P - wheel with potentiometric wire   E - gear
S - scale   F - recording camera   G - mirror galvanometer
R - sensitivity reducer
L - polarographic lamp.   H - pressure regulator for the analyzed gas
D - sintered glass plate

Measurements were made at a pressure of 50 mm water column at the exit. As can be seen in Figure 4. the height of the limiting current decreases with increasing rate of flow of the electrolyte.

The determination of the influence of varying SO_3 concentrations was not easy. Therefore the SO_2 gas, before it was mixed with air, passed through a wash bottle containing oleum, and thus the gas entering the absorption vessel contained, apart from the SO_2 also SO_3 in the form of mist. In this way a series of measurements with varying SO_2 concentrations was made in the presence of SO_3 mist. Graphical presentation of the height of the limiting current as a function of SO_2 concentration is a line, and therefore it is possible to conclude that SO_3 does not interfere with the analysis.

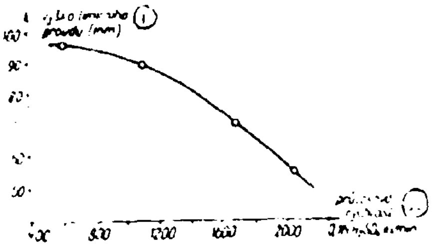

Figure 4. Limiting Current as a Function of the Rate of Flow of the Electrolyte

Key: 1: Height of limit current in mm
2: Flow velocity ml/min

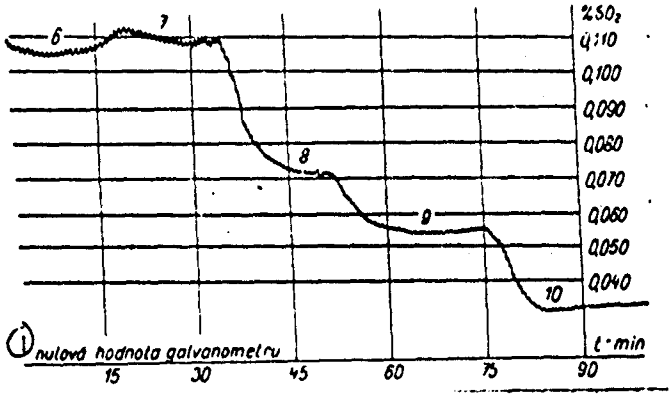

Figure 5. Recordings Made in the Limits 0.02 - 0.1% SO_2

Key: 1. Zero value of the galvanometer

3. Calibration of the Instrument for Concentrations of SO_2 Within the Limits 0.02 - 0.1 Percent

The calibration was made with synthetic mixtures of SO_2 and air by using suitable orifice plates to obtain an SO_2 concentration of 0.1 percent (determined iodometrically). Later, after a 15- or 20 minutes interval the SO_2 concentration was reduced by increasing the air pressure. During the recording, after stabilization of the limiting current, a sample was taken simultaneously for iodometric determination of SO_2. Measurements were taken at a potential of 4 V at the battery, sensitivity of the galvanometer 1/40, imposed potential 1.0 V, pressure of the gas entering the absorber 50 mm water column, flow rate of 0.1 N-H_2SO_4 25 ml in 25 minutes.

The heights of the limiting current, plotted as a function of the SO_2 concentration, show a linear relation.

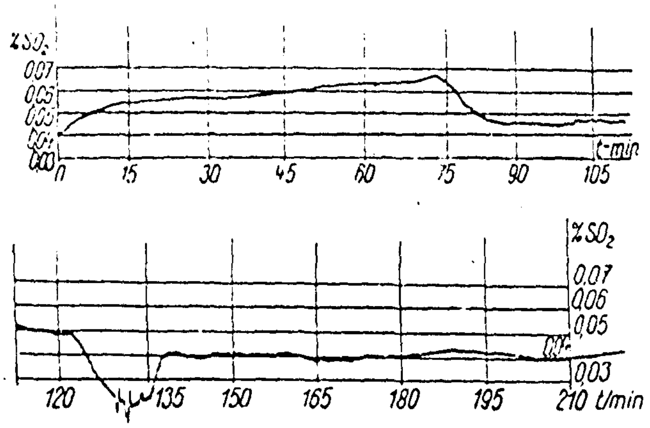

Figure 6 & 7. Time Profile of SO_2 Concentration in the Exit Gas After Absorption in Zinc Sulfite

4. Practical Tests of the Analyzer in Determination of SO_2 After Absorption in Zinc Sulfite

The instrument was calibrated for concentrations in the range of 0.02 - 0.1 percent SO_2, and tested practically for continous analyzing of SO_2 gas at the exit from an absorption vessel containing zinc sulfite, into which 0.33 percent SO_2 gas was introduced; into the absorber at definite time intervals (at the beginning after 70 to 120 minutes) a calculated amount of $Zn\ (OH)_2$ was introduced; the details of the experimental arrangement of the absorption are given in the article of J. Srbek[1]. Imposed voltage, rate of flow of electrolyte, the pressure of the gas entering the absorber, and all the other constants used during the calibration remained unchanged. The results of measurements are compared in Table I. with those found iodometrically.

Table I.

Tabulka I

① Měř. čís.	② Doba uvádění plynu v min.	③ % SO_2 ve výstup. plynu		⑥ Výtěžek SO_2 v %
		④ Jodometr.	⑤ polarograf.	
1	0 — 15	0,018	0,018	85,5
2	20 — 35	0,054	0,055	83,4
3	45 — 60	0,072	0,062	81,2
4	81 — 97	0,050	0,048	85,5
5	105 — 120	0,040	0,048	85,5
6	125 — 145	0,047	0,041	87,6
7	150 — 165	0,047	0,041	87,6
8	170 — 185	0,050	0,043	87,0

Key: 1. Experiment No.
2. Period of introduction of gas in minutes
3. % SO_2 in exit gas
4. Iodometrically
5. Polarographically
6. Yield of SO_2 in %

The table shows a good agreement between the results obtained by the two methods.

The recorded curve shows the changes in the SO_2 concentration in the exit gas in a more illustrative way.

The shape of the curve shows clearly first:

a) The increase in the SO_2 content of the exit gas up to about the 72nd minute (2 min. delay compared to addition of $Zn(OH)_2$), then after the addition of Zn hydroxide the value drops to nearly the original figure.

b) That the influence of the addition of $Zn(OH)_2$ (at the 120th min) is deformed by a fault in the supply of SO_2. that is pure air was passing through the absorber for a certain period of time. The fault, otherwise disagreeable, was a favorable opportunity for the apparatus, which quickly reacted to the change and drew attention to it.

Apart from this practical use of the analyzer, it was also used with success for the measurements of SO_2 after absorption in calcined magnesite, and for the measuring of SO_2 before absorption.

Conclusions

The experiments showed that:

1. The height of the limiting current is a linear function of the concentration of sulfur dioxide.

2. The height of the limiting current decreases with increasing rate of flow of the electroylte.

3. Sulfur trioxide does not influence the analysis

The apparatus can be used for calibration of the scales of sulfur dioxide concentrations as a function of the intensity of the current from empirical observations; in this way eventual errors due to oxidation of SO_2 to SO_3 are eliminated.

Because of the linear shape of the function it may be deduced that this oxidation has very little effect upon the measurements, that is, that it does not take place to any significant extent.

The laboratory analyzer was arranged for continuous recording lasting several hours, and was calibrated for SO_2 concentrations in the limits 0.02 - 0.1 percent. It was practically tested in measurements of SO_2 after absorption in a suspension of $Zn(OH)_2$ during a study of possible uses of sulfur dioxid in waste gases. The results of the measurements were compared to values found iodometrically, and a good agreement between the two methods was found.

The photographic polarographic recording must be considered as a temporary laboratory expedient that is not quite suitable for production purposes. The problem will be developed further, to remove this shortcoming, and find a solution acceptable to the needs of production and research.

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