

Determination of Atmospheric Sulfur Dioxide by Coulometric Titration

1. INTRODUCTION

Sulfur dioxide monitors have been designed that utilize conductivity or acidity produced through its oxidation to form sulfuric acid. In general, such instruments lack specificity. Colorimetric methods such as the West-Gaeke procedure, have been adapted for use in continuous monitors. Although this approach may provide excellent sensitivity and selectivity, the instruments require considerable maintenance. Monitors utilizing coulometry for the measurement step, although subject to some interferences, offer advantages of general instrument reliability. Such instruments may be quite sensitive and precise.

2. SCOPE AND FIELD OF APPLICATION

The method is applicable to most urban or industrial atmospheres provided particulates and the interfering species such as O_3 , halogens, H_2S , and strong oxidants are removed by suitable scrubbing (11.5). The response time is 3-5 minutes to reach 95% of the final value. Sulfur dioxide levels as low as $10.5\mu\text{g}/\text{m}^3$ (4ppb) can be detected, but the normal working range is $262\mu\text{g}/\text{m}^3$ to $104,800\mu\text{g}/\text{m}^3$ (0.1ppm to 40ppm).

3. DEFINITIONS

3.1 *Cell electrolyte*

The solution with appropriate buffers containing the titrant ion.

3.2 *Supporting electrolyte*

All chemical species in the cell electrolyte except the titrant.

3.3 *Titant*

Species in the electrolyte which is depleted by the introduction of SO_2 . Normally it is I_3^- or Br_2 .

4. PRINCIPLE

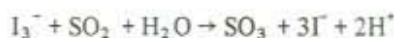
An air sample of known volume is pulled through suitable filters to remove particulates and interferences. The resultant gas stream is fed into an enclosed coulometric cell. The SO₂ reacts with the titrant in the cell electrolyte causing a decrease in the titrant, and the amount of current required to bring the titrant back to its original level is measured on a recorder. By Faraday's law the number of microequivalents of SO₂ can be determined and the SO₂ level expressed in the $\mu\text{g}/\text{m}^3$.

In the method described no sample preparation is required. The air stream of approximately 150ml/min is pulled through a dust filter covered with a stainless steel mesh (to prevent the intake of large objects or insects) (11.5) and a scrubbing filter (11.5) into the cell electrolyte. Two electrodes measure the redox potential originating from either Br₂/Br⁻ or I₃/I⁻ couple depending on the commercial system employed. As SO₂ is drawn into the enclosed coulometric cell, the titrant's concentration is lowered. The new potential is compared to an internal reference and the difference is converted into a current between two other electrodes (generating electrodes) in the coulometric cell. The amount of current required to bring the titrant concentration back to its original value (potential) is monitored. The amount of SO₂ titrated is found from a calibration curve, and related to the atmospheric concentration by noting the time interval of measurement and the flow rate.

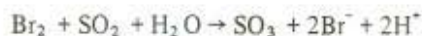
5. REACTIONS

Depending on the commercial coulometric cell employed, the supporting electrolyte composition will vary. Several typical half reactions are:

Cell reaction:



or



Generation anode reaction:



or



6. REAGENTS

As specified by manufacturer for the cell electrolyte.

7. APPARATUS

Many coulometric titration systems for SO₂ are available. Beckman, Dohrman and Phillips instruments are representative of this field.

8. SAMPLING AND SAMPLES

Atmospheric air requires no preparation other than passing it through a dust and scrubbing filter.

9. PROCEDURE

9.1 *Safety precautions*

Follow normal precautions for handling of caustic materials (cell electrolyte).

9.2 *Calibration curve*

A SO₂ permeation tube of known capacity is employed to provide a source of SO₂. To set up a calibration curve atmospheric air is pulled through the dust filter, an activated charcoal filter, past the permeation tube, through the scrubbing filter and into the coulometric cell at a constant flow rate. The cell electrolyte is stirred to disperse the SO₂ uniformly and thus increase the mass transfer.

Due to evaporation in the course of analysis a certain amount of titrant is lost and this produces a small current. To compensate for this evaporation current, atmospheric air is pulled through a dust filter, activated charcoal filter, scrubbing filter and into the coulometric cell. Since this air is free of reactants, the evaporation current can be determined and subtracted from the gross SO₂ current providing a net current curve.

9.3 *Determination*

An air sample is pulled through a dust filter and scrubbing filter. The resultant air stream is passed into the coulometric cell and the current recorded.

Using the same flow rate and time interval of measurement the evaporation current can be determined and subtracted from the gross current leaving the net current due to SO₂. By comparison to the net current curve the amount of SO₂ titrated can be found, and expressed as $\mu\text{g}/\text{m}^3$.

9.4 Blank tests

Since the cell is reset to its original state in the course of measurement, no blank tests are necessary.

10. EXPRESSION OF RESULTS

$$\mu\text{g}/\text{m}^3 = \frac{(Q_G - Q_E)k}{v \times t} \times 10^{-6}$$

- where Q_G = Number of coulombs in sample titration at standard flow rate & time
 Q_E = Number of coulombs due to evaporation current during standard flow rate & time
 v = flow rate, ml/min
 t = time in min of test sample
 k = constant from net calibration curve;
 $\mu\text{g SO}_2/\text{coulomb}$

11. NOTES ON PROCEDURE

11.1 The filtering system employed in the measurement process ensures that most interfering species are removed. Of those that remain in NO_x is the most prevalent. By using a buffered solution (pH = 7) the NO_x effect can be minimized. In the I_3^-/I^- system sodium azide has been used to selectively react with any Cl_2 or NO_x reaching the supporting electrolyte.

11.2 Temperature control is necessary in the coulometric cell. Most cells are kept at approximately 35° .

11.3 Air flow can be varied while a normal flow is approximately 150ml/min. A representative system is capable of titrating $5\mu\text{g}$ of SO_2 in 3 to 5 minutes.

11.4 Precision of titration is limited by the precision of sample introduction. Constant flow rate is thus very important.

11.5 A heated glass fiber filter can be used as the dust eliminator. In this way all gaseous components are allowed to flow through. The silver filter would remove the ozone, halogen, and H_2S interferences, and in some systems it is used as the scrubbing filter. In the I_3^-/I^- system only the strong oxidant methyl hydroperoxide and peroxyacetic acid interfere, but the probability of finding these compounds in the atmosphere is low.

12. SCHEMATIC REPRESENTATION

- 12.1 Pull the atmospheric sample through heated glass fiber filter.
- 12.2 Pull resultant gas stream through Ag scrubbing filter.
- 12.3 Pull resultant stream into stirred coulometric cell.
- 12.4 Record flow rate, time interval, and current.

13. REFERENCES

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