

Chapter 1

Introduction

Sulphur is the thirteenth most abundant element on Earth. Natural sulphur can be found in ores, minerals, coal petroleum, and volcanic ash. Today, sulphur contained products include fertilizers, surfactants, detergents, insecticides, fungicides, polymers, drugs and gasoline. Sulphur appears in various form such as sulphur, sulphide, sulphate, sulphite, thiosulphite and thiosulphate.

The analysis of sulphur usually arises out of industrial, agronomic, environmental or social interest. From the environmental point of view, the sulphur dioxide has been known to have contributed about 20% of total air pollutants¹ and seriously endangering human health. In most analytical determinations, sulphur is first converted to sulphate, which is the most stable form for quantitative analysis. For the determination of sulphur in organic compounds, the organically bound sulphur is converted to one of the sulphur-containing ions, usually the sulphide and sulphate ions. This can be done by either combustion in a stream of oxygen² or reduction in a stream of hydrogen³. In wet combustion methods²⁻⁵ sample pretreatment including fusion with sodium peroxide⁶, combustion in an oxygen-filled flask⁷ and potassium fusion method^{8,9} are used to prepare inorganic sample for sulphur determination.

Sulphate determination in the above mentioned decomposition products can be done by a wide range of methods: gravimetric¹⁰⁻²⁰, titrimetric²¹⁻³¹, complexometry^{27,31,332-34}, colorimetry^{31,35}, turbidimetry³⁶⁻⁴⁰, continuous flow injection turbidimetry⁴¹, nephelometry^{31,42,43}, ring oven method⁴⁴, chromatography⁴⁵, coulometry³¹, potentiometry⁴⁹⁻⁵³, amperometry⁵⁴⁻⁵⁶, conductometry⁵⁷⁻⁶², polarography⁶³⁻⁶⁶, ion selective electrode (silver/silver sulphide⁶⁷, fluoride⁶⁸,

barium⁴⁹), high frequency conductometric titration⁶⁹, AutoAnalyzer⁷⁰, ultra-violet spectrometry^{71,72}, indirect flame atomic absorption spectrophotometry⁷³⁻⁷⁵, direct flame spectrometry^{76,77}, atomic emission spectrometry⁷⁸⁻⁸¹, molecular emission spectroscopy⁸²⁻⁸³, time resolved molecular emission spectrometry⁸⁴, spectrophotometry⁸⁵⁻⁹¹, spectrofluorimetry^{92,93}, flame photometry⁹⁴⁻⁹⁷, radiometry⁹⁸⁻¹⁰⁰, X-ray analysis^{101,102}, and neutron activation analysis¹⁰³.

Coulometry is based on Faraday's Law which inter-relates electrical current, equivalent weights and time. Faraday's Law stated that the total quantity of chemical change produced at the electrodes of a cell is directly related to the quantity of electricity passed through (in Coulombs). The amount required for one gram of equivalent weight of electrochemical change is 96487 Coulombs, which is equivalent to one Faraday.

There are two types of coulometric analysis – by the application of a controlled potential to the cell or by the passage of a constant current through the cell. Szelbelldy and Somorgi¹⁰⁴ developed the process of constant current coulometry. In this process, a chemical generated by the passage of a constant current through the cell, reacts with the sample in solution. The end-point can be indicated by many methods such as potentiometric, amperometric, conductometric and colorimetric. An electrical switch is used as the burette stop-cork.

Coulometric method has been extensively used for the determination of sulphur compounds such as sulphur in hydrocarbon¹⁰⁵⁻¹⁰⁷ and steel¹⁰⁸⁻¹⁰⁹. This method also been used for the determination of sulphur dioxide in the atmosphere¹¹⁰⁻¹¹¹ as

well as in gas mixtures¹¹²⁻¹¹³. The advantage of this method is selectivity, rapidity, wide range of analytical application, and ease of automation. However, the cost of performing the above mentioned technique is high as it involves expensive equipment.

In nephelometric measurement, sample is illuminated by an intensive beam of power I_0 . The power of the scattered light at right angle to the initial beam, I_{90} , after passing through a scattering analyte of length l is measured. The ratio of I_{90}/I_0 increases with the increasing number of particles in suspension¹¹⁴. In general, the intensity of the scattered light is directly proportional to the concentration of the particles in the light path. A relationship has been written by Ewing¹¹⁴,

$$I_{90}/I_0 = k_{90} c,$$

where k_{90} is an empirical constant for the system and measurement must be carried out under identical conditions. Nephelometric measurement is useful in measuring micro amounts of substances such as the sulphate ion. The limitation of this technique is that the above-mentioned relationship holds only if the scattering centres are sufficiently dilute to make any secondary scattering negligible in the forward direction. Both ultraviolet and visible spectrophotometric and nephelometric methods have been commonly used in the determination of sulphate ion.

Indirect flame atomic absorption spectroscopy can be readily performed using a conventional atomic absorption apparatus for determination of sulphur. This technique is based on direct chemical reaction with an equivalent amount of metal which is then determined by atomic absorption spectroscopy. The first method reported is based on the precipitation of barium sulphate on addition of excess barium

chloride to the sample solution. The precipitate is dissolved in disodium EDTA solution and the resulting barium concentration is determined at 553.5nm in an air-acetylene flame¹¹⁵. This method is used to estimate sulphur content in urine, diet, faeces and biological tissue after oxidation.

Ametani¹¹⁶ used a similar method to determine sulphur content in nickel arsenide type of sulphides and sulphospinels. Also, Galindo¹¹⁷ used it to determine soil-sulphur in volcanic ash derived soils. In situation where the necessity to dissolve the barium sulphate precipitate have to be avoided, a known excess of barium is added to the sulphate solution and the excess is determined after the precipitation of barium sulphate¹¹⁸. This method is used to determine sulphur content in textiles¹¹⁹, potable water¹²⁰, polluted water¹²¹, acidic sulphate soils¹²² and organic materials¹²³. The very slight solubility of the barium sulphate precipitate is compensated by calibration against sulphate standard solution treated in similar manner as the sample.

Classical chemical methods such as gravimetric and titrimetric methods still play an important roles , even though the above mentioned modern techniques and instruments suitable for precise and accurate chemical analyses. Calibration standards (i.e. thiourea, anhydrous sulphanilanic acid, sulphanilamide and sulphonol) for these instruments are in turn assessed by conventional classical methods. Hence, with appropriate refinement on experimental procedures and apparatus used, these classical methods will fulfill its roles both in routine analysis and as a means of calibration standard used in these instrumental methods.

Gravimetric and titrimetric methods of analysis are based on the measurement of the amount of reagent that combines with an analyte. Gravimetric analysis is concerned with transformation of the element to be determined into a pure and stable compound, which can be readily converted into a suitable form for weighing. The gravimetric method of sulphate determination, is employed in routine sulphur content analysis for dry rubber¹²⁴ and effluents¹²⁴ sample. The advantage of gravimetric over titrimetric analysis is that the constituent is isolated and thus may be examined in the presence of impurities. But, this method is time-consuming and tedious to perform compared to titrimetric method.

In view of the short comings of the gravimetric methods, titrimetric determination of sulphate has become the chosen method in many laboratories. The determination of sulphate by titrimetric method is based on the stoichiometric formation of stable barium sulphate precipitate. Sulphate content can be determined by titration with barium chloride solution in an alcoholic medium, using Alizarin Red S indicator¹²⁵. The optimum concentration of alcohol found to be 30-40%. Lower or higher concentration of alcohol caused the end-point to be less distinct. Wagner¹²⁶ and Alicino¹²⁷ carried out the titration in 80% alcoholic medium with barium perchlorate, using Thoron with added methylene blue as indicator, and the end-point was quite sharp.

Budensinsky¹²⁸ has recommended sulphonazo III as a more superior indicator compared to Thoron. Sharper colour changes from red to blue is more readily observed, and is not affected by changes of pH. Hozumi and Umemoto¹²⁹ have compared the use of Thoron, arsenazo III and sulphonazo III as indicator in such

titration and found that arsenazo III gave the best end-point. The sulphate was determined by adding excess barium perchlorate and back titrated with sulphuric acid. Budensinsky and Krumlova¹³⁰ carried out the titration in acetone medium using dimethylsulphanazo III as indicator. Budensinsky⁸⁵ found that dimethylsulphanazo III is superior than Thoron and sulphonazo II in his subsequent study. Other indicator used in the sulphate titrations with barium ion include tetrahydroxyquinone¹³¹, dibromosulphonazo III^{130,132}, carboxyarsenazo^{130,133}, dinitrosulphnazo III^{130,134}, and chlorophosphanazo III⁸⁵.

Titrimetric method is simple and its slight solubility can be compensated through calibration using standard sulphate solution. The titrimetric method is undoubtedly suitable for simple and pure samples. However, this method suffers several draw-backs when a complex sample is analysed. As a result, it is the objective of this work to look into the various problems encountered in the direct titrimetric determination of sulphate.

This present work used dimethylsulphonazo III as indicator based on the preliminary investigation carried out by Budensinsky⁸⁵ and Tioh³¹. This work includes a preliminary investigation of solvents used in the direct tirimetric determination of sulphate, a preliminary investigation of the effects of foreign interfering ions and an attempt to remove of phosphate interference in the barium perchlorate titration of sulphate .