Identification And Estimation of Micro Amounts of Some Inorganic Ions

A Thesis
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GENERAL INTRODUCTION

INORGANIC MICROANALYSIS

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Microanalysis is the branch of microchemistry which deals with the application of the available microtechniques to the development of small scale analytical methods. These analyses involve separation, detection, and estimation of minute amounts of materials by different techniques.

1. Separation :

The importance of analytical separation cannot be minimized even with the development of instrumental methods. The problem of interferences is still of great significance, masking has become the standard tool for eliminating interferences. It is suitable way for avoiding the tedium of physical separation. Solvent extraction, ion exchange, volatilization and even precipitation are considered essential for the ultimate exploitations of inorganic analytical processes. Sachdev and West[1] have proposed a method for separation and determination of a number of metals by extraction of metal dithizonates with ethyl propionate. Matthews and Riley[2] have developed an anion exchange scheme for specific separation of microgram amounts of thallium in the study of silicate rocks, marine sediments, and sea water[3]. Thin layer chromatography is finding increase application in microanalysis, e.g. separation of the chelates of copper, cobalt, nickel and iron[4] and also noble metal separation[5].

The ring oven technique introduced by Weisz[6] in 1954 is a remarkably simple, yet elegant technique. Although there is a number of papers dealing with this method, its potential value in applied chemistry, as well as in teaching has been generally overlooked. Klockow and Bohmer[7] used the ring oven technique for the radiochemical separation of ^{144}Pr from ^{144}Ce and Ghose and Dey[8] have described a method for separation and microdetermination of Al, In, Ga and Tl in a single drop of the test solution.

2. Qualitative Tests :

Spot test methods make up, the bulk of references dealing with qualitative analysis. Feigl[9] has reviewed the chemistry of spot tests especially with regard to specificity, selectivity and sensitivity. West and Hamilton[10] have shown that the characteristics of spot test are greatly dependent on the nature of the reaction medium. Various spot tests for use in identifying alloys have been summarized by Wilshaw[11], while Monk[12] has reviewed the development of electrographic analysis.

Weisz and Klockow[13,14] have used the ring oven in the identification and semiquantitative determination of radionuclides. It has been used in combination with other techniques, e.g. solvent extraction[15], spectrophotometry[16] and thin layer chromatography[17,18].

Infrared spectra have sometimes been used for the qualitative analysis of inorganic compounds and the salts of polyatomic ions can often be identified[19,20] by the position and intensities of the absorption bands.

3. Quantitative Methods

A substance can often be determined by a variety of methods, and the analytical chemist generally can save much time and improve the accuracy of results by critical comparison of the various methods which might possibly be applied. The essential characteristics of a method, namely, accuracy, sensitivity, and selectivity, must always be considered, but other criteria such as cost of equipment and duration of analysis are also of great practical significance. The choice of a method of determination depends first on the nature and amount of sample available and, second on the sensitivity and accuracy required. The methods of analysis could be classified into two main categories, one is the non-instrumental methods which involve usually titrimetric procedures using different reagents. For microanalysis, the titration may be preceded by amplification methods in which the small amount of the ion to be determined is amplified to another ion found in larger concentration,$^{21-24}$ or may be instrumental methods which involve the use of special instruments which measure a particular property characteristic of the ion under test. Instrumental methods may also be classified into the following:

i- Emission spectroscopic methods

These methods produce characteristic emission spectra which are specific for a particular element. The spectra may involve the outer electrons as in flame arc, and spark spectroscopy and fluorimetry, whereas X-ray fluorescence methods utilize the electron in the K, L, ... shells. Activation analysis evolved γ-rays of specific energies and these involve the nuclear particles. The disadvantages of flame, arc, and spark spectroscopy are the costly equipment, limitation and the time required for complete analysis. Fluorimetric methods of analysis are based on the measurements of the fluorescence radiation emitted by ions in solution under ultra-violet irradiation. X-ray fluorescence is used for the determination of many heavy metals. The sensitivity is often too low but is advantageous in that it is a non-destructive method. Apart from being a costly method, its application is limited to only heavier metals. Activation analysis allow the simultaneous determination of a number of elements. They are sensitive and accurate but require very sophisticated apparatus for counting and computing the results, apart from the equipment required for activation.

ii- Absorption spectrophotometric methods

A different type of analysis is the so-called absorption spectroscopy which is based on the absorption of certain quanta of energy necessary for excitation of electrons. For the irradiation of the solution or the substance, a very wide range of wave-lengths is available. Light from tungsten lamp or hydrogen lamp gave absorption spectra in visible and U.V. regions, respectively.

These methods are used in colorimetry and spectrophotometry. In atomic absorption spectroscopy, the source is a cathode lamp which gives absorption bands at various ranges of wave-lengths.

In some cases of micro-analysis, the spectrophotometric or colorimetric methods represent only a final step as a finish for the analytical method. They are preceded by some chemical reactions involving the production of a substance which is examined spectrophotometrically.

The present investigation is an attempt to provide some new analytical methods for the analysis of micro-amounts of some inorganic ions. The techniques used in these methods include spot tests, ring oven, colorimetry, spectrophotometry and amplification methods. The literature relevant to every method has been included in the next chapters.

CHAPTER I

A NEW SPOT TEST FOR CYANIDE ION AND CYANOGEN GAS

A NEW SPOT TEST FOR CYANIDE ION AND CYANOGEN GAS[*]

Introduction :

The detection of small amounts of cyanide ions and cyanogen gas are important because of their extreme toxicity to living matter. Cyanides are used in electroplating, in precious metal refining, in case of hardening of steels and in many other processes; in the gas industry, many atmospheres and effluents contain cyanides and cyanogen gas, e.g., the effluents from coke ovens and other gas making plants. Hydrogen cyanide is used extensively as a rapid and conveniently applied fumigant for food storage plants, such as warehouses and the holds of cargo ships.

The literature is rich with methods for the detection of cyanide ions. Cyanide reacts with ammonium polysulphide to form thiocyanate[25-28] which produces a blood red colour by addition of ferric chloride. The test is applicable in the presence of sulphide or sulphite (sensitivity,$1\,\mu g$ CN^-; concentration limit,

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1:50,000). Another extremely sensitive test for cyanide depends on the formation of prussian blue[26,29-32] ($Fe_4[Fe(CN)_6]_3$). The copper acetate benzidine test[33] is also used and this is sensitive to 0.25 μg CN^- in a dilution limit of 1:200,000[9] . The reaction involves the oxidation of benzidine to benzidine blue brought about by the removal of copper (I) from copper (II) copper (I) system. This raises the oxidation potential of the system resulting in the oxidation of benzidine.

The ability of the cyanide ion to form stable complexes and cause de-masking of inner complex-bonded transition metals has also been utilised by various workers for detecting the cyanide ion. Feigl and Feigl[34] reported a colorimetric procedure in which the de-masking of dimethylglyoxime by the action of cyanide on the palladium dimethylglyoximate complex permits the nickel ion present to form a red dimethylglyoximate. An advantage of this test is that it can be made in alkaline solution, and in contrast to other methods, does not require the previous liberation and evolution of hydrogen cyanide. Other palladium complexes gave analogous results, and compared with palladium dimethylglyoximate, the palladium salt of 1,2-cyclohexanedione-dioxime[35] gave an increased sensitivity.