CHAPTER I

INTRODUCTION

A number of methods are available for analytically difficult separations. Some of the more important are solvent-extraction, thin layer chromatography, gas chromatography, ion exchange and electrophoresis. Solvent-extraction has received increased attention during the last few years. The more important developments in this field have been the use of computer technique (1), the use of N-benzoyl-N-phenyl hydroxylamine in the determination of zirconium and hafnium (2) and the separation of molybdenum (VI) from rhenium (VI) with pentyl acetate (3). Systematic studies of solvent mixtures for the separation of alkaline earths (4) and for the extraction of zinc oxinate (5) should also be mentioned. However, the largest number of studies have been made in which solvent extraction has been combined with spectrophotometry (6-18).

Chromatography continues to attract attention and some novel techniques have been developed recently.
The separation and identification of group I, II and IV cations by thin layer chromatography on maize-starch is particularly interesting (19, 20). Phosphates have been separated on circular layers of corn-starch (21), while halides and metal-rhodizonates have been separated on silica-gel (22,23). The most significant development in this field is, however, the introduction of molecular-sieve chromatography. In this technique widely different materials such as silica-gel (24), calcium phosphate (25), and the Bio-Gel range of polyacrylamides (26,27) have been used. This technique has, recently, been used for the separation of phosphates (28). Electrophoresis also leads to a number of interesting separations (29,30). Thorium and uranium have been separated as their oxalate complexes (31). Cello-gel strips have combined the advantage of gel and electrophoresis (32) and their use is bound to be exploited in the near future. The use of electrophoretic spectra for the identification of aromatic substances has also considerable novelty (33).

For separations of ions, the ion exchange method is the most efficient. In this method cations may be separated using mixed or complex-forming eluents. Thio-cyanate-based eluents are particularly efficient (34).
Liquid ion exchangers have been used to treat silica columns (35) and to use the silica-gel so obtained for thin-layer chromatography (36). The use of synthetic inorganic ion exchangers has not received much attention as this field is still in its infancy. However, by preparing different inorganic ion exchangers and by studying the Kd values of different anions and cations on these ion exchangers a number of useful separations should be possible (37-50).

After separation the ion can be more easily detected or determined. Chalmers and Dick (51) have developed analysis schemes combining solvent-extractions and spectrophotometry. Similarly, circular thin-layer chromatography has been employed (52) for a rapid identification of group I-IV cations after group separation has been affected by classical procedures. Sometimes it is possible to develop methods of detection for inorganic ions and organic substances which do not need any prior separation. For instance spot tests have been developed for silver (53,54), antimony (55-57), thorium (58), mercury(II)(59), arsenic (56,57), tin (56), glyoxal, pyruvic acid, lactic acid (60), copper (61) formanilide, benzoin (62), and zinc (63). The basis of these tests
is either complex formation or ordinary chemical reaction. Therefore, those ions will be difficult to detect, by this procedure, which have weak complex-forming ability. No wonder that few spot tests have been described for non complex-forming ions such as Li\(^{+}\), Na\(^{+}\), K\(^{+}\), Cs\(^{+}\), Rb\(^{+}\), and Hg\(_2\)^{2+}. It is therefore necessary to spend some effort for developing effective procedures for the detection of these ions.

After the contents of a mixture have been separated and qualitatively detected, the problem of quantitative determination arises. Sometimes separation is achieved from all interfering substances, but more often such a complete separation is not possible. Under these circumstances selective methods of determination have to be developed (64-98). Selectivity is generally achieved by complexing the interfering substances. Only occasionally a reagent is described which reacts specifically with the substance to be determined (99,100). Amongst the ions to be determined Fe\(^{3+}\) is one of the most important as it occurs in plant, animals, soils, and alloys. Even though very good methods have been developed (101-109) for the determination of iron, its determination deserves and is receiving considerable attention. And it is worthwhile
to evolve simple procedures which are fast and relatively free from interferences. Existing methods can sometimes be modified (106,110) to increase the selectivity and the sensitivity of the determination.

It was with these objects in view that the present work was undertaken. A new synthetic inorganic ion exchanger has been prepared and the $K_d$ values for various metal ions have been determined. Further studies on this material may lead to better methods of separation of various ionic materials. A new method has been developed for the detection of a non-complexing ion i.e. $\text{Hg}^{+2}$ ion. This method is specific and sensitive and applicable in common analytical situations. A fast, simple and selective procedure has also been proposed for the determination of iron. The idea is to separate or complex most of the interfering ions before the actual determination is performed. Attempts have also been made to use mercurous nitrate for the selective detection of unsaturated organic compounds. In the following pages are summarized the results, the methods of approach, and the chemistry of the reactions involved for the solution of the problems mentioned above.
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