CONCLUDING REMARKS

One of environmental analytical chemist’s major challenges is the analysis or determination of the elements concerned with pollution and other environmental problems. The essentiality and toxicity of many elements has forced the environmental analytical chemist to take cognizance of these and other elements in his analytical scheme. Sound environmental analytical chemical measurements are essential to provide the data needed to ensure the quality of the environment and the health of the public. Analytical techniques are quite invaluable in environmental assessment to ensure that the damage to environment is not excessive or to assess the extent of damage. Analytical measurements also help in the monitoring of remediation procedures. Moreover, since environmental matrices are quite complex and consist of various constituents, quality assurance and method validation are quite important.

Of the various criteria used in selection of an appropriate trace analytical method, simplicity, sensitivity, accuracy, precision and selectivity are of prime importance. Other important considerations such as scope, sampling, standard requirements, cost of equipment and time of analysis are of practical importance. Spectrophotometric method is one such analytical technique which meets our requirements.

It is evident from the literature that in spite of large number of visible spectrophotometric methods reported for the determination of the elements of environmental interest, many of them suffer from one disadvantage or the other, such as low sensitivity, poor selectivity, usage of strong acid medium, instability of the system, low range of determination, critical working conditions, involve complicated procedures, use of hazardous organic solvents for extraction, etc. The chemical reactivity of many of the elements have not been exploited thoroughly for the purpose of designing sensitive, accurate and facile spectrophotometric procedures for the analysis of elements of environmental interest. Besides, the choice of a chromogenic reagent has to be considered in proper perspective. Thus, analysis of the elements needs improvements in the analytical procedures from time to time due to the multiplicity of the problems in the environmental samples.

These aspects motivated the investigator to develop simple, sensitive, selective, reliable and economical spectrophotometric methods for the determination of some selected elements of environmental interest [As, Be, Ce, Cr, N-NO₂⁻, and Se] and their analysis in various environmental matrices.
In the present investigation, the investigator has made sincere attempts to find suitable, readily available, inexpensive and common reagents for the spectrophotometric determination of selected elements in their pure forms and in the various environmental samples containing them and succeeded in developing useful visible spectrophotometric procedures for As, Be, Ce, Cr, N-NO₂⁻, and Se by exploiting the characteristic chemical properties of these elements. The details of systematic investigations, optimization of procedures, sensitivity, selectivity, precision, accuracy and chemistry involved through analogy or probability, carried out in developing new procedures for the spectrophotometric determination of the cited elements with a few readily available chromogenic reagents, are incorporated in different chapters of the thesis. The thesis presents the different spectrophotometric methods based on the author’s analytical practices, to assist analysts in obtaining data of requisite quality and to aid in the evaluation of the quality of reported data. The major findings of the present study are summarized in the following paragraphs.

Two simple and sensitive spectrophotometric methods have been developed for the determination of arsenic. The reduction of potassium iodate by arsenic(III) in acidic medium to generate iodine, which oxidizes LMG to MG dye is the basis for its analysis. The method is simple and highly sensitive, though it involves heating step for complete oxidation of LMG to MG. In the second method, arsenic(III) reacts with iodine monochloride in acidic medium to liberate iodine, and the unreacted ICl iodinates the dye, Thymol Blue. A linear increase in absorbance with increasing arsenic(III) concentration was observed. The absorbance measured at 535 nm corresponds to the concentration of uniodinated Thymol Blue. The method is simple and sensitive. Another feature of the new methods is that associate or common interfering ions were not found to have any serious influence on the colour system, thus making the new methods more suitable. The developed methods have been successfully applied to the analysis of arsenic in various environmental samples.

A ternary complex formation is the basis for the analysis of beryllium with haematoxylin in the presence of a cationic surfactant, cetyltrimethylammonium bromide. The absorbance of the formed ternary complex was measured at 592 nm with a molar absorption coefficient of \(7.07 \times 10^4\) L mol\(^{-1}\) cm\(^{-1}\). The method is highly sensitive, reliable and involves more simple procedure for beryllium determination, but it requires 1 h for the complete complex formation. The method has been successfully applied to the determination of beryllium in water samples.

Two different chromogenic reagents (LCV and LMG) have been proposed for cerium determination in environmental and high-purity rare-earth oxide samples. In both the methods
Ce(IV) quantitatively oxidizes LCV to CV and LMG to MG. The developed methods are simple, selective, sensitive, but require heating for complete oxidation of the respective dyes.

A direct spectrophotometric determination of chromium with PCPM, based on the oxidation of PCPM by chromium(VI) in acid medium is described. The method is simple and sensitive (ε = 2.09 × 10^4 L mol\(^{-1}\) cm\(^{-1}\) at 535 nm), but susceptible to some of the associated ions. However, they are obviated by the use of appropriate masking agents prior to its analysis. The second method deals with an indirect spectrophotometric determination of chromium. The method involves two steps, the first step is oxidation of hydroxylamine to nitrite by chromium(VI), whereas in the second step, the generated nitrite diazotize with PNA followed by coupling with CZA. The method is facile, sensitive, selective and reproducible. Both the methods were applied to the analysis of chromium in various samples.

The formation of bisazo dye by diazotization followed by coupling reaction of nitrite with 4-amino azobenzene and acetyl acetone has been spectrophotometrically measured at 500 nm (ε = 4.2 × 10^4 L mol\(^{-1}\) cm\(^{-1}\)) for the analysis of nitrite. The diazotization requires no cooling to 0 – 5 °C. High stability of the bisazo dye and elimination of extraction steps are versatility of the method. Moreover, the reagents used are inexpensive. In another method, Thionin has been used for the indirect determination of nitrite. A decrease in absorbance of the dye at 600 nm due to diazotization of the primary amino group with nitrite was measured (ε = 4.1 × 10^4 L mol\(^{-1}\) cm\(^{-1}\)). Both the methods are simple, sensitive, rapid and cost-effective, and the methods were successfully applied to nitrite determination in water and soil samples.

Highly sensitive spectrophotometric methods have been developed for the analysis of selenium in water, soil, plant material and synthetic cosmetic samples. In the first method, the iodine liberated by the reaction between Se(IV) and KI in acidic medium quantitatively oxidizes LMG to MG (ε = 1.67 × 10^5 L mol\(^{-1}\) cm\(^{-1}\) at 615 nm). In the second method, selenium reacts with KI in an acid medium to liberate iodine which is then bleaches the dye, Safranine-O at 532 nm (ε = 8.21 × 10^4 L mol\(^{-1}\) cm\(^{-1}\)). This was the basis for an indirect and accurate determination of selenium.

A parallel determination with reference methods (standard methods in few cases) was carried out for each of the developed method and the results obtained were compared and subjected to the statistical analysis in order to validate the developed methods. The performance of the methods developed was judged by calculating the Student’s t- and F-tests. At 95% confidence level, the calculated F- and t-values do not exceed the theoretical values. Therefore, a comparison of the values obtained revealed that there is good agreement between the values.
obtained from the reference and proposed methods in the analyses of As, Be, Ce, Cr, N-NO₂⁻ and Se. The reliability of the methods was checked by the method of standard addition to the samples of test and by recovery experiments. The sensitivity of each method was ascertained through molar absorption coefficient, Sandell’s sensitivity, Beer’s law limits and optimum photometric range. The regression analysis using the method of least-squares was made for slope, intercept and correlation coefficient obtained from different concentrations. The data obtained in the determination of each selected element with different reagents are summarized in text as well as in tables at appropriate places. The selectivity of each proposed method was ascertained through interference studies with other associated ions that are usually present in environmental samples.

An overall comparison of the several methods proposed for the spectrophotometric analyses of studied elements of environmental interest reveals that, all the methods are equally superior as they exhibit molar absorption coefficient values of $\geq 10^4$, good linear ranges, and excellent sensitivity.

All the developed methods have been compared with some of the reported methods available in the literature. The comparison revealed that the proposed methods are simple and more sensitive to many of the existing methods. Therefore, the proposed methods can be used as alternate methods to reported ones and provide a wide choice for the routine determination of aforementioned elements depending upon the situation. This study has provided apparently novel methods for the analysis of chosen elements in various samples.

Finally, the following overall conclusions can be drawn from the developed methods for the analysis of the selected elements of environmental interest. The developed new spectrophotometric methods are simple, inexpensive, rapid, reliable, selective, sensitive, specific, precise and accurate over the many existing methods, and the methods uses easily available chromogenic reagents. The successful applicability of the proposed procedures for the analysis of the elements in various samples shows the utility of the method. In addition, the present study demonstrates that the low cost of the technique, ease of handling, lack of need for consumables, and almost no maintenance have caused spectrophotometry to remain a popular and essential technique over the many sophisticated and expensive techniques available for the determination of chosen elements at trace levels, particularly in the laboratories of developing countries with limited budget.