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Investigation of Interferences Effecting Environmental Chemistry Experiments

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In this study, it was aimed to investigate physical and chemical interferences for different devices and methods commonly used in environmental studies. In experiments carried out with spectrophotometer, physical interference caused from colour was investigated for phenol, ammonium, cyanide, nitrite and fluoride analyses. It was observed that colour caused deviations of 23.20, 35.07, 40.35, 279.38 and 125.00 % for phenol, ammonium, cyanide, nitrite and fluoride, respectively. The interference of sulphate was also examined in sulphide analyze, by using spectrophotometer. Results were found 40 times more because of sulphate interference. In experiments carried out with flame atomic adsorption spectrophotometer and inductively coupled plasma (ICP) interferences of metal ions were investigated in different matrixes. Furthermore by using conventional method, interference of chloride was examined in chemical oxygen demand (COD) determination. Chloride caused deviations after 500 mg/L in experiments carried out with various chloride concentrations.

Key Words: Interference, Spectrophotometer, ICP, AAS, Chemical oxygen demand.

INTRODUCTION

Spectrophotometer, atomic adsorption spectrophotometer and inductively coupled plasma (ICP) are commonly used devices in waste water characterization studies. In order to investigate the light adsorption of material, UV and visible region adsorption spectrophotometers are used[1]. Most anions, all metals and many physical and aggregate properties can be determined by colourimetric techniques, which are fast and cost effective[2]. The method may, however, be unreliable for dirty and coloured samples. Turbidity and colour are among the most important reasons causing interference for this device.

The atomic spectrometry techniques are extensively employed for the quantification of metallic species. Among these techniques, flame atomic absorption spectrometry presents desirable characteristics, such as low costs, operational facilities, high analytical frequency and good selectivity. However, the direct determination of trace metals by this technique is generally difficult because of matrix interference problems and low concentration of metals in samples[3]. The determination of metal ions at low concentration levels is very important in the context of clinical diagnosis, geo-chemical explorations and environmental protection. Their enrichment, before determination with flame AAS or ICP-AES is usually required[4].

Metals can also be conveniently determined by emission spectroscopy using inductively coupled plasma (ICP). A great advantage of ICP emission spectroscopy as applied to environmental analysis is that several metals can be determined simultaneously by this method. Thus, multielement analysis of unknown samples can be performed rapidly by this technique. Another advantage is that, unlike atomic absorption spectroscopy, the chemical interference in this method is very low[5]. There are many fields in which the available sample volume is the limiting factor for an elemental analysis. Over the last 10 years, sample introduction systems used in plasma spectrometry (*i.e.*, inductively coupled plasma atomic emission spectrometry, ICP-AES and mass spectrometry, ICP-MS) have evolved in order to expand the field of applicability of these techniques to the analysis of micro- and nanosamples[6].

Beside instrumental techniques, conventional methods are also commonly used for determination of pollution parameters. These conventional methods are based on volumetrical or gravimetrical studies. Chemical oxygen demand (COD) is a representative example for parameters which are generally determined by using conventional methods[7].

Both for instrumental applications and conventional methods, accuracy of results is very important for defining and solving problems. Factor effecting accuracy can be classified as personal mistakes, method faults and errors coming from the instrument. Interferences, an important reason of incorrect results, are assessed as method faults. Especially samples in waste water analyses have matrix structures. Element that is required to be analyzed should be separated from this matrix structure in order to obtain correct results.

In this study, effects of physical interferences coming from colour were investigated for phenol, ammonium, cyanide, nitrite and fluoride analyses by using spectrophotometer. The interferences in heavy metal determination were also investigated by using ASS and ICP. Furthermore, chemical interferences were examined in sulfate and COD analyses by using spectrophotometric and conventional methods.

EXPERIMENTAL

In this study, Cadas 200 model spectrophotometer was used. This device can make measurements at the range of 190-900 nm wavelength for ultraviolet and visible region by using a single beam source. Lange cuvette tests were used during experiments made with Cadas 200 spectrophotometer. Related wavelengths and other setting were saved into instrument in order to make measurements automatically after required reaction time.

Varian SpectrAA model flame atomic adsorption spectrophotometer was used in the experiments. Atomization, the most important part of these analyses, was achieved by using air-acetylene flame.

Spectro Ciros CCD model ICP was used. Plasma was formed with argon gas in ICP technique. In this system plasma reaches high temperatures ranging between 1000-6000 K by adsorbing energy from magnetic region and provides optimum atomization.

General procedure: Phenol, sulfate, cyanide and nitrite analyses were carried out in a sample prepared from treatment sludge of pharmaceutics sector. 100 g of dried, grained and sieved sample was added to distilled water. Eluate was prepared after 24 h extraction period[8]. A turbid, brown mixture was obtained. Interferences coming from colour were investigated in this sample. Fluoride analysis was achieved in a sample with red colour, taken from metal coating sector. Sulphide analyses were made in waste waters of textile industry.

In experiments made for showing the effect of chloride in COD analyses, 1 N stock NaCl solution was prepared. By using this stock solution 100, 500, 1000, 1500 and 2000 mg/L NaCl solutions were obtained. Chloride contents of prepared solutions were determined by Argentometric method[9].

Stock solutions of 1000 mg/L concentration were prepared for tested metals (Ni, Cu, Zn, Cr, Fe, Ni).

Detection method: Interferences occurred during phenol, ammonium, cyanide, nitrite, fluoride and sulphide analyses were investigated by using spectrophotometer.

In phenol analysis, phenol in the sample reacts with 4-nitroaniline to form a yellow colour complex, which is then measured in a photometer. Phenol is determined at 476 nm in spectrophotometer. In ammonium measurements, ammonium ions react at pH 12.6 with hypochlorite ions and salicylate ions in the presence of sodium nitroprusside as a catalyst to form indophenol blue. It is determined at 694 nm lightwave.

During cyanide analyses cyanides react with chlorine to form cyanogen chloride, which in turn reacts with pyridine in the presence of barbituric acid, condensing to form a violet colourant. It is detected at 588 nm. Nitrites react with primary aromatic amines in acidic solution to form diazonium salts. These combine with aromatic compounds that contain an amino group or a hydroxyl group to form intensively coloured azo dyes. Nitrite is measured at 515 nm wavelength. Fluoride ions react with zirconium to form a colourless zirconium fluoride complex. This causes the red zirconium lake which is present to lose colour. Fluoride is detected at 588 nm. In sulphide analyses, the reagent reacts with sulphide to form a yellow complex. Sulphide is determined at 435 nm. COD parameter was determined according to standard method 5220 B by using open reflux method.

Interferences in metal analyses were studied by using flame AAS and ICP. In order to form the calibration curves of nickel, copper and iron; solutions with 0.5, 1.0 and 2.0 mg/L concentrations were prepared by using 1000 mg/L stocks of required metals. By using these solutions, calibration curves were drawn in ASS for Ni, Cu and Fe at 232, 324.7 and 248.3 nm wavelengths, respectively. In studies carried out with ICP, Fe was analyzed at 239.562, 259.940 and 275.573 nm wavelengths whereas copper was analyzed at 324.759 and 219.226 nm wavelengths.

RESULTS AND DISCUSSION

In the study, effect of interference coming from colour was investigated for phenol, ammonium, cyanide and nitrite analyses by using spectrophotometer. This interference was removed by subtracting blank value from the results. Colour of the sample caused deviations of 23.2, 35.07, 40.35 and 279. 38 % for phenol, ammonium, cyanide and nitrite, respectively. These interferences are presented in Figs. 1-4. As seen from figures, colour causes an important interference for the investigated samples. Especially in nitrite analysis this deviation reaches high values (Fig. 4).

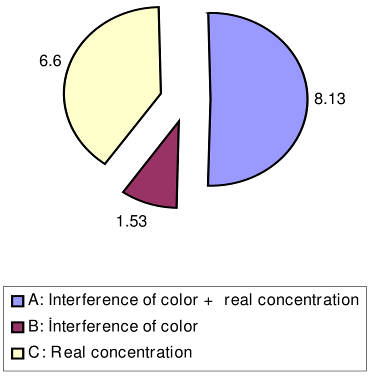


Fig. 1. Interference of colour in phenol analysis

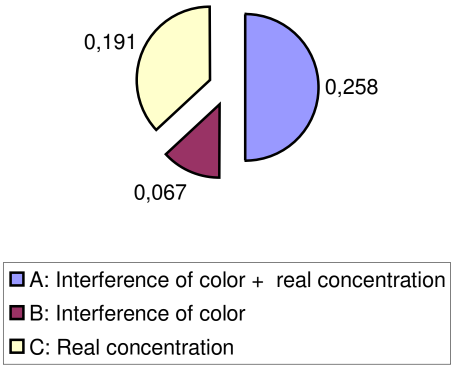


Fig. 2. Interference of colour in ammonium analysis

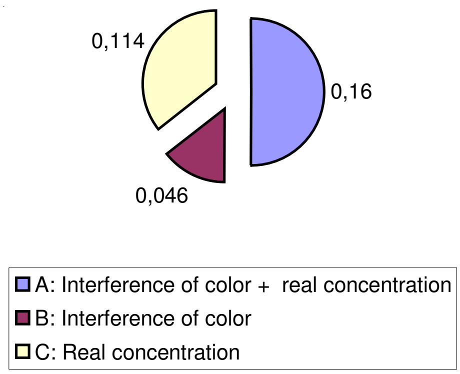


Fig. 3. Interference of colour in cyanide analysis

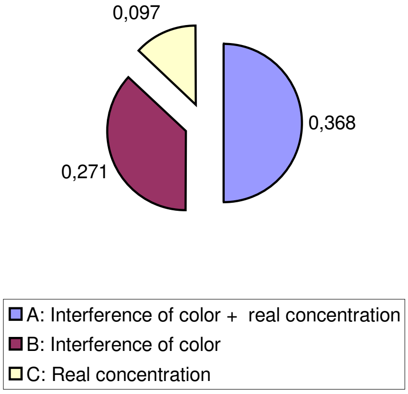


Fig. 4. Interference of colour in nitrite analysis

Effect of colour on fluoride analysis was investigated by using another sample taken from metal coating sector. Inference levels caused by colour were monitored with measurements made before and after distillation. As seen from Fig. 5, fluoride concentration was determined as 450 mg/L before distillation whereas it decreased to 200 mg/L after distillation. This result shows that colour causes a deviation of 125 % for the investigated sample.

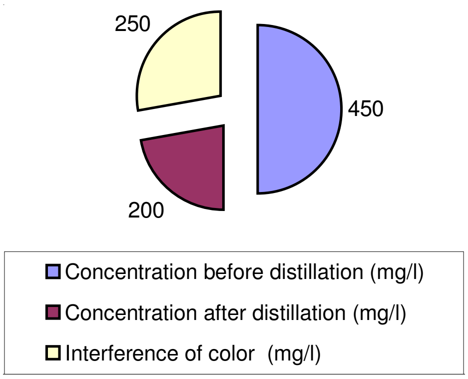


Fig. 5. Interference of colour in fluoride analysis

In spectrophotometrical measurements, experimental studies were concentrated on chemical interferences. Some elements or groups affecting the signal of analyzed element cause chemical interference. In order to give an example of this situation, we have investigated the effect of sulphate on sulphide analyses. As seen from Fig. 6, sulphide value was determined as 7.26 mg/L in the sample containing 40 mg/L sulphate whereas this value decreased to 0.18 mg/L after the dilutions making sulfate concentration lower then 5 mg/L. Sulphate concentrations higher then 5 mg/L formed a white precipitate and caused turbity in the sample. This turbidity caused a great deviation in the analysis. Sulphide was determined 40 times higher then the correct value. It is pointed out that chemical interference is an important source of errors in experimental studies.

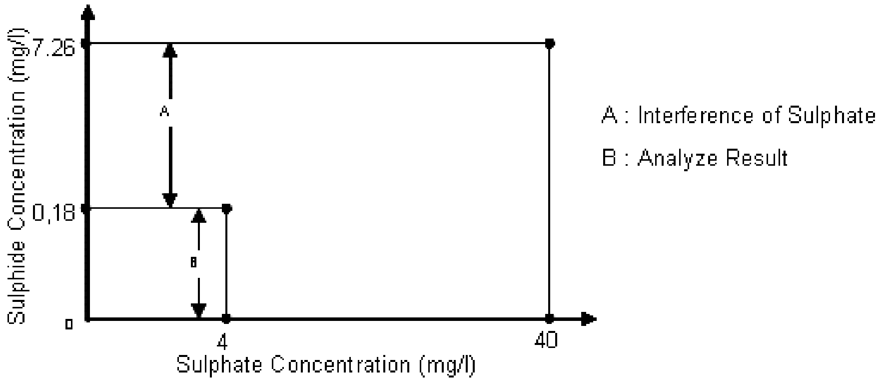


Fig. 6. Interference of sulphate in sulphide analysis

Chemical oxygen demand (COD) is an important parameter commonly used for wastewater characterization. In COD determination, chloride causes interferences causing errors in results. During COD experiments, ferrous ammonium sulphate reacts with dichromate as shown in the equation below[10]:

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O \quad (1)$$

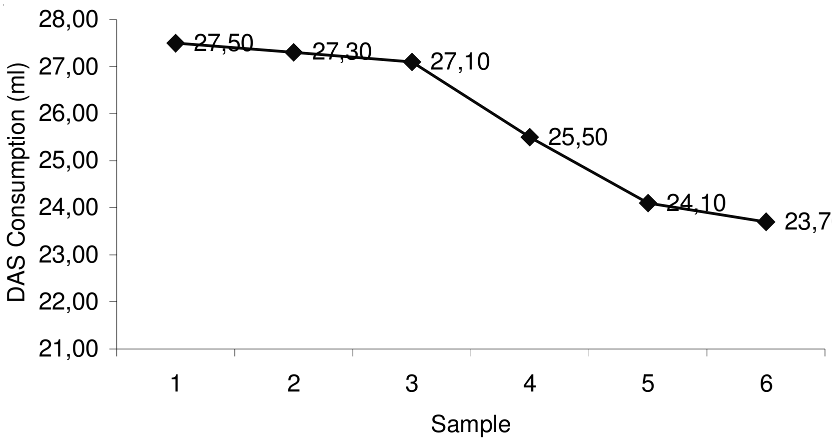
Ferroin indicator changes into red colour when all dichromate is reduced to Cr^{3+}. But in the presence of chloride Cr_2O_7 reacts with Cl^- ions:

$$6Cl^- + Cr_2O_7 + 14H^+ \rightarrow 3Cl_2 + 2Cr^{3+} + 7H_2O \quad (2)$$

Furthermore Cl^- ions can also react with AgCl, a common catalyst of COD experiments and forms precipitate causing turbidity:

$$Ag^+ + Cl^- \rightarrow AgCl \quad (3)$$

In order to investigate the chloride interference in COD analyses, oxidation was achieved in samples containing 100, 500, 1000, 1500 and 2000 mg/L chloride. Effects of chloride interference occured after 500 mg/L Cl concentration (Fig. 7). Highest deviation was seen at the sample containing 2000 mg/L chloride. This interference caused 13.81 % decrease in DAS consumption. As seen from this example chloride is an important reason of interferences in COD analyses and should be removed from the samples absolutely.



1. Sample with no chloride content
2. Sample with 100 mg/L chloride content
3. Sample with 500 mg/L chloride content
4. Sample with 1000 mg/L chloride content
5. Sample with 1500 mg/L chloride content
6. Sample with 2000 mg/L chloride content

Fig. 7. Chloride interference in COD analysis

In nickel analyses carried out with AAS, interferences of copper and iron were investigated. As seen from Figs. 8 and 9, in addition of 1 mg/L copper solution to 1 mg/L nickel solution, 37.69 % increase was determined in concentration. This ratio remains stable for the following additions. In the case of iron addition, a positive interference was noted by increasing iron concentrations.

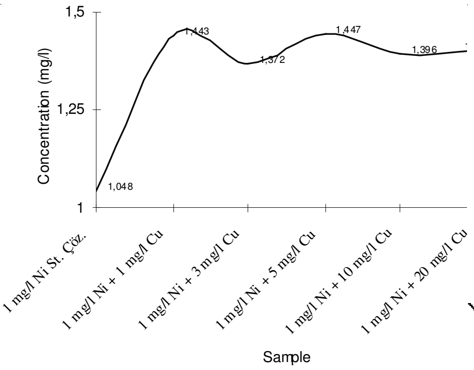


Fig. 8. Copper interference in nickel analysis for AAS system

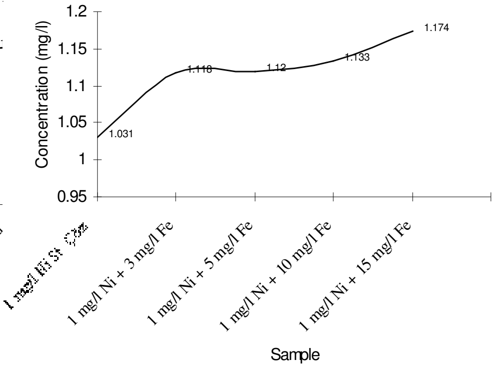


Fig. 9. Ferrium interference in nickel analysis for AAS system

Also in copper analyses, effects of zinc and chromium inferences were examined by using AAS. As seen from Figs. 10 and 11 zinc and chromium did not cause any interference in copper determinations.

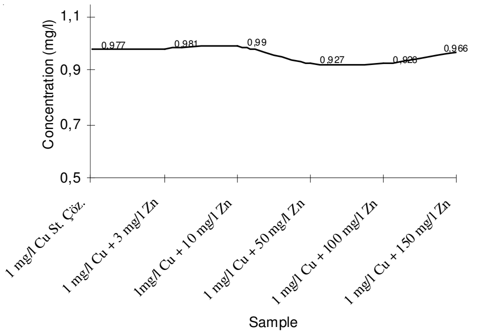


Fig. 10. Zinc interference in copper analysis for AAS system

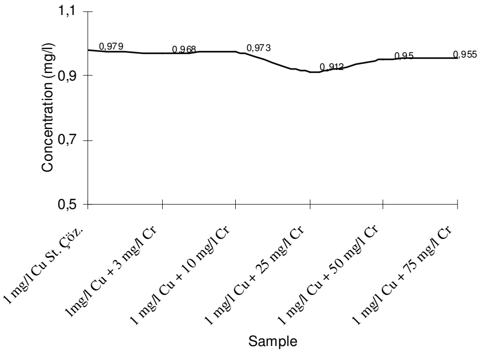


Fig. 11. Chromium interference in copper analysis for AAS system

Nickel and tin interferences were investigated for iron analyses in AAS system. Inference caused by nickel and tin addition has increased with increasing concentrations in iron analyses (Figs. 12 and 13).

In iron analyses carried out with ICP, interference occurred at 239.56 nm among three tested light waves. At 239.56 nm, nickel interference has started at 50 mg/L concentration and highest deviation (negatively % 32) was seen at 75 mg/L level (Fig. 14). Furthermore in copper analyses with ICP systems, no interference was occurred by zinc addition at all tested light waves Fig. 15.

Conclusion

Before starting environmental chemistry studies, a comprehensive literature survey should be achieved in order to mark possible interferences. Determined

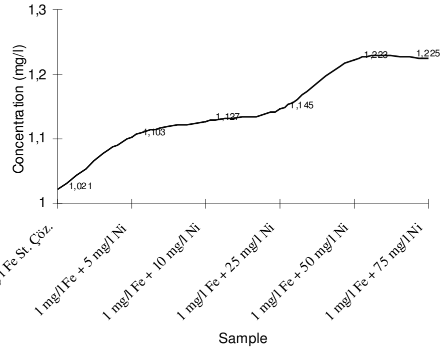


Fig. 12. Nickel interference in iron analysis for AAS system

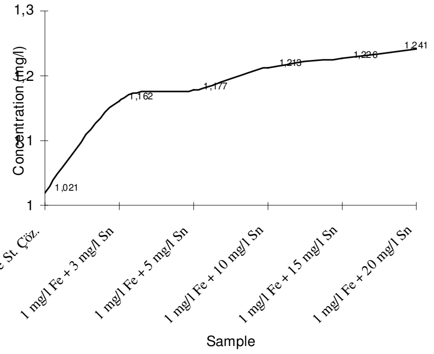


Fig. 13. Tin interference in iron analysis for AAS system

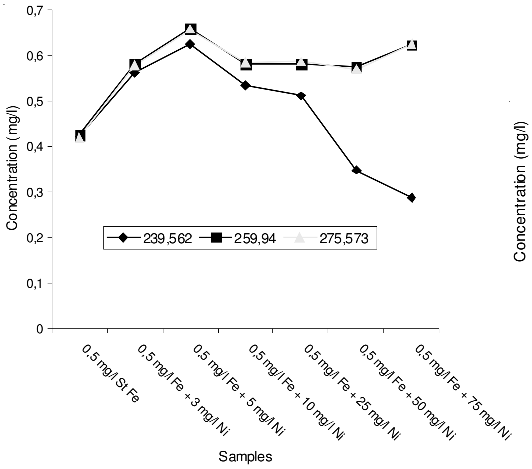


Fig. 14. Nickel interference in iron analysis for ICP system

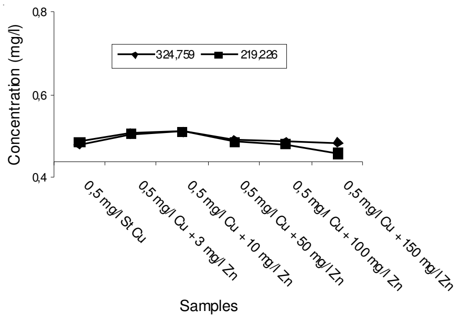


Fig. 15. Zinc interference in copper analysis for ICP system

interferences should removed by appropriate methods before measurements. Especially for studies on potable and drinking water, removal of interferences carries importance as quality limit values are very low. In spectrophotometrical analyses, colour interferences should be removed with methods like filtration, centrifugation or distillation. The possible errors can also be prevented by determining absorbance of colour. Chemical interferences can be removed by diluting the sample. Another way of preventing interferences is to add any chemical reacting easily with the interfering element. In COD analyses interference of chloride can be removed by adding mercury sulphate. Chloride can be bound to Hg^{2+} ions according to following reaction: $Hg^{2+} + 2Cl^- \rightarrow HgCl_2$. There are several methods used for preventing interferences for metal determinations in AAS systems. First of all by dilutions, low concentrations causing no interference can be obtained. Another method is masking the interfering material. It means adding a chemical actively reacting with interfering elements.

But absolutely, the best way of preventing interference is standard addition. In this method removal of interfering material is not aimed. Interfering material effects the added standard in a similar way so that we can obtain the effect of inference accurately. Interferences seen in ICP systems are less compared to AAS systems. By using ICP systems an element can be measured in different wavelengths. So interference can be removed by changing wavelengths.

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