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RESEARCH ARTICLE

ANALYSIS OF SOME HEAVY METALS LEVEL IN ISPARTA'S DRINKING WATER USING UV SPECTROPHOTOMETRY AND PRINCIPAL COMPONENT REGRESSION

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Abstract

Background: Heavy metals, which are likely to be found in natural water samples, can cause some discomfort when taken into the body in high amounts. The aim of this study is to create complexes of iron, copper and cadmium, which are major heavy metals that can be found in natural water samples, with ammonium pyrrolidine dithiocarbamate (APDC) chelate, to analyze these complexes with UV-spectrophotometry after the optimum conditions to be created in water samples, and to apply the principal component regression chemometric method to the data obtained here.

Method: In the applied spectrophotometric method, complexes of each heavy metal were first formed with APDC. Then, appropriate mixtures of these complexes were prepared and their spectra were recorded. Principal component regression chemometric method was applied to the data obtained.

Results: Very consistent results of the chemometric method applied to the data obtained in the spectrophotometric analysis of the complexes of the heavy metals studied after providing optimum conditions were observed.

Conclusion: It can be stated that the method developed in the research and the chemometric method applied to the data obtained from here can be easily applied in routine water analysis.

Keywords: APDC, cadmium, chemometric method, copper, iron, principal component regression.

INTRODUCTION

Nowadays, quality control of drinking water is of great importance. Surface water or groundwater intakes are often used for drinking water production. Good and safe drinking water should not only meet sanitary requirements, but also be tasty, clean, and free of sediment and bad odor. In drinking water, there are three major pollutants: those resulting from industrial and agricultural pollution resulting from water distribution and storage, water treatment processes[1]. One of these is metals and metalloids that can cause health problems such as cancer in humans. Some metals and metalloids, such as zinc, iron, selenium, chromium, cobalt, vanadium or copper, are essential elements for proper growth of humans, but their excess accumulation in the body can cause undesirable consequences. On the other hand, some metals such as lead and cadmium also play a negative role in metabolic activities and may have toxic effects on body tissues. Inorganic pollutants are among the most hazardous water pollutants because they have unique properties such as chemical stability, poor degradation (decomposition), wide range of sources, high toxicity, and bioaccumulation and remediation difficulties.

In this study, ammonium pyrrolidine dithiocarbamate (APDC) chelate was used to determine some heavy metals that may be found in drinking water. The purpose of APDC is to create the solid phase of the metals under investigation and to form shethals with metal ions. For this reason, the recoveries of the chelating product APDC and Pb, Cu and Cd metals were examined.

APDC (ammonium pyrrolidine dithio carbamate) is a chelate with strong anti-oxidation that can form complexes with metal ions via the amine group attached to sulfur, as shown in Figure 1. With this feature, it is widely used as an analytical reagent in the formation of different metal complexes, especially in atomic absorption spectrophotometry[2-4], ICP-MS[5,6], fluorescence spectroscopy[7], atomic fluorescence[8], spectrophotometric[9,10] and HPLC[11] methods. Malissa and Schöeffmann[12] were the first to investigate APDC. The melting point of the pure ammonium salt of APDC is 149-152°C. APDC has been used to co-precipitate many metals at various pH values. It forms water-insoluble complexes with many metals. It does not work with alkaline and alkaline earth elements. Selectivity can be achieved by adding reagents such as EDTA, tartrate, citrate or cyanide to the elements in which it does not work[13].

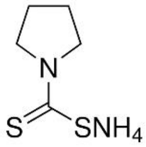

Figure1: Molecular structure of APDC.

Due to the possible harmful effects of heavy metal ions found in drinking water on human health and additional environmental toxicity, it is important to develop sensitive, simple and reproducible analytical methods for the detection of such potentially harmful metals. For this purpose, when we search the literature for the combined determination of copper, lead and cadmium, many methods come to our attention. These include atomic absorption spectrophotometry (AAS)[1416], inductively coupled plasma mass spectrometry (ICP-MS)[17,18], high pressure liquid chromatography[19], spectrometry[20], X-ray absorption spectroscopy[21] and Raman spectroscopy[22].

Developments in chemometric studies in recent years have led to the development of multivariate calibrations to easily solve the complex systems we encounter. With these methods, components in samples containing more than one component can be easily determined quantitatively using many wavelengths[23]. The aim of this study is to determine some heavy metal ions found in the same environment together by forming complexes. In individual determinations of heavy metals, during separation and masking, some of the species that may be present in the matrix environment are at least partially similar to the analyte, and some analyte may be removed from the environment during the separation process. In both cases, one may be faced with the fact of making mistakes[24]. Therefore, in this study, synthetic matrix environments in which these three heavy metals coexist were created and their determination was successfully made using the principal component regression method, which is a powerful chemometric method, without any preliminary separation.

MATERIALS AND METHODS

Apparatus

In this study, the spectra of the solutions prepared under optimum conditions were obtained using the UV 1700 PHARMASPEC SHIMADZU spectrophotometer. The obtained spectrum values helped to determine the amounts of copper, lead and cadmium in drinking water and to evaluate the results chemometrically.

Chemical and reagents

Chemicals of analytical purity were used in the experiments. The substances used are lead acetate trihydrate, cadmium acetate dihydrate and copper nitrate trihydrate copper (II) nitrate, hydrochloric acid used for pH studies, potassium chloride, acetic acid, sodium acetate, ammonium chloride and ammonia substances are pure substances of Merck and Aldrich brands. Stock solutions of all substances, 1 g/100 mL, were prepared and experiments were carried out based on these substances; 2 g APDC was weighed and dissolved in a small amount of methanol to make up to 100 mL.

Method

In our study, the most appropriate parameter studies of the complexes we would create were first carried out (ligand amount, pH, waiting times and the relationship between metal concentration and absorbance) and optimum conditions were provided. After this, the spectra of each heavy metal were taken, first one by one, and then the mixtures prepared in different proportions. The obtained data were evaluated by the PCR calibration method. During this process, pure substances were taken from the stocks, with concentrations between 2-10 ppm, the solutions were prepared by completing the total volume to 25 mL, and absorbance readings were made in UV spectroscopy. Later, since each substance gives a maximum at a different wavelength, absorbance readings were made in UV spectroscopy of synthetic mixtures created from pure substances, and the substances were examined next to each other without the need for any preliminary separation. In the last step, the prepared synthetic sample solutions were examined. Subsequently, the validated method was applied to water samples.

RESULTS AND DISCUSSION

Amount of Ligand

APDC (ammonium 1-pyrrolidine dithiocarbamate) was selected as the complexifier in the study. In order to decide on the optimal amount of ligand in the formation of Pb^{+2}-APDC, Cu^{+2}-APDC, Cd^{+2}-APDC complexes, 20-60 times more than the amount of metal solution used by adding APDC, 6 spectrum results were obtained on the spectrophotometer device and the results obtained were evaluated on the graph as shown in Figure 2, Figure 3, and Figure 4 and decided on 60 times more as the optimal amount of ligand.

Optimum pH

After the optimum ligand amount is decided, 1 ml of 10 ppm metal solution is taken and 60 times the amount of APDC (0.6 ml) metal solution is added to find the optimum pH value. The spectrum values of the solutions created with various buffer solutions are taken and interpreted in the spectrophotometer and the optimum pH value is determined. Since the highest and most stable absorbance’s were obtained at pH 10 in the analyzes of the solutions created between pH 6 and 10, as seen in Figure 5, Figure 6, and Figure 7, pH 10 was decided for the complexes formed.

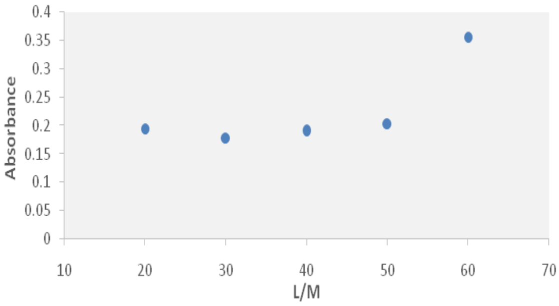

Figure 2: Effect of ligand amount on the formation of Pb^{+2}-APDC complex.

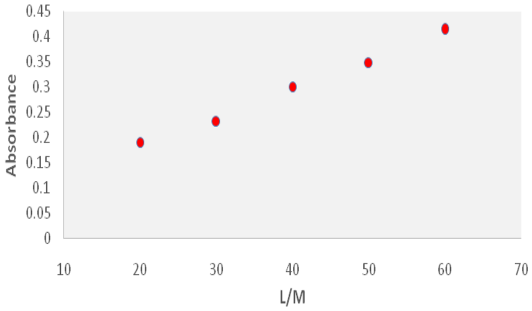

Figure 3: Effect of ligand amount on the formation of Cu^{+2}-APDC complex.

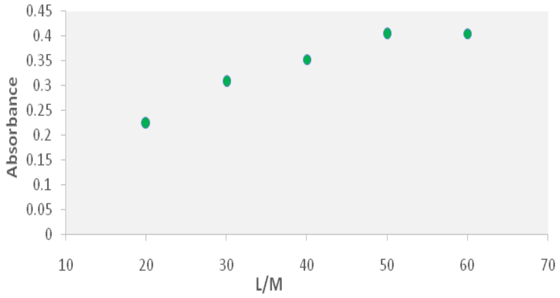

Figure 4: Effect of ligand amount on the formation of Cd^{+2}-APDC complex.

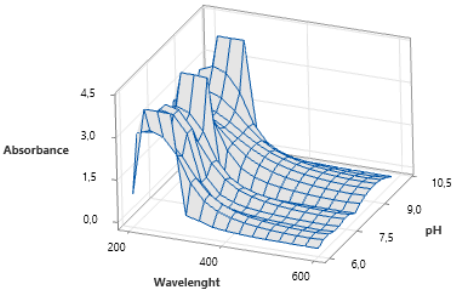

Figure 5: Effect of pH on the formation of Cu^{+2-}APDC complex.

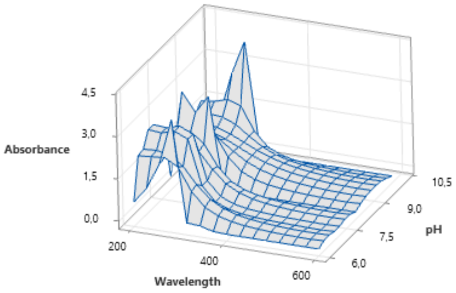

Figure 6: Effect of pH on the formation of Pb^{+2-}APDC complex.

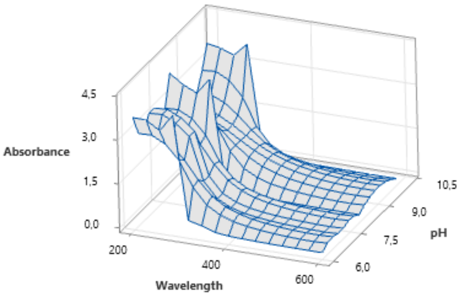

Figure 7: Effect of pH on the formation of Cd^{+2-}APDC complex.

Holding time

In order to reach the optimum holding time after having the optimum ligand amount and optimum pH value, 1 ml of the 10 ppm metal solution is taken, APDC is added as much as 60 times more than the metal solution, and the obtained solutions are kept for 10-60 minutes by using the pH 10 buffer and transferred to the blank solution in the spectrophotometer device. The response was read and the values were obtained. Based on the obtained values, it was decided that the optimum holding time would be 10 minutes, as seen in Figure 8, Figure 9, and Figure 10.

Metal concentration - absorbance relationship

After determining the optimum ligand amount, pH value and holding time, solutions were prepared to maintain these conditions and the metal concentration-absorbance relationship was investigated. Of the 10 ppm metal solutions, 0.125, 0.250, 0.375, 0.5, 0.625 ml corresponding to 0.5, 1.0, 1.5, 2.0, 2.5 pmm, respectively, were taken and complexizer and pH buffer were added and the spectrum was taken on a spectrophotometer. As shown in Table 1, the wavelength at which each metal complex gave the maximum absorbance, calibration equation and correlation coefficient were determined.

Optimization of spectral conditions

In spectrophotometric studies, it was decided that 0.1 M HCL solvent was the appropriate solvent for this research for Pb^{+2}-APDC, Cu^{+2}-APDC, Cd^{+2}-APDC. Spectra of Pb^{+2}-APDC, Cu^{+2}-APDC, Cd^{+2}-APDC complexes and their corresponding mixture in 0.1 M HCL were taken in the wavelength range of 305-445 nm (Figure 11).

As can be seen Figure 11, all three compounds gave spectrum values in the same wavelength range. Therefore, since it would not be possible to quantify all three compounds at the same time with classical spectroscopic processes, the PCR chemometric method was used.

Calibration and validation

In hydrochloric acid, which we use as a solvent for chemometric calibrations, 0.1-0.4 ppm for Pb^{+2}-APDC, 0.1-0.4 ppm for Cu^{+2}-APDC, 0.1-0.7 ppm ranges for Cd^{+2}-APDC. Total 32 different calibration sets were prepared, including three compounds in. The reason for choosing symmetric calibration in our study is to minimize errors that may occur during analysis.

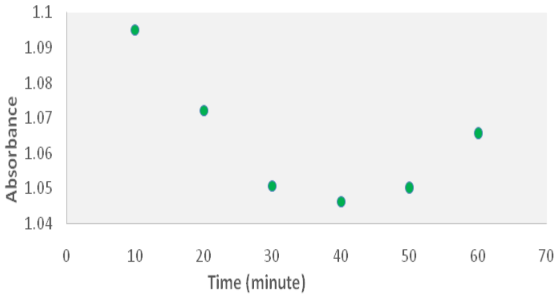

Figure 8: Effect of holding time on the formation of Pb^{+2}-APDC complex.

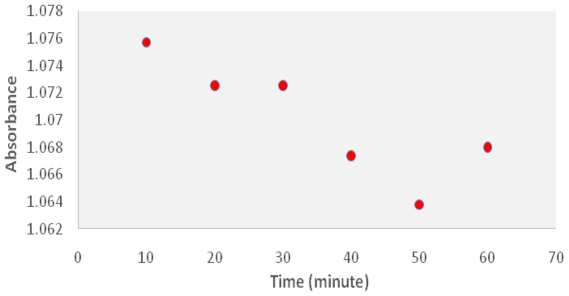

Figure 9: Effect of holding time on the formation of Cu^{+2}-APDC complex.

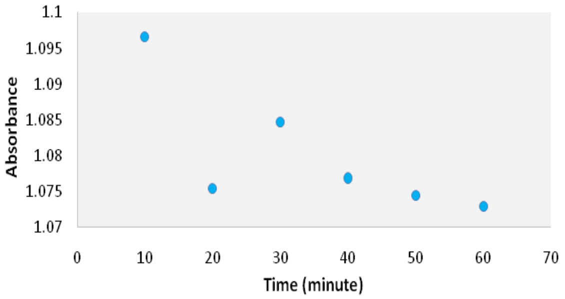

Figure 10: Effect of holding time on the formation of Cd^{+2}-APDC complex.

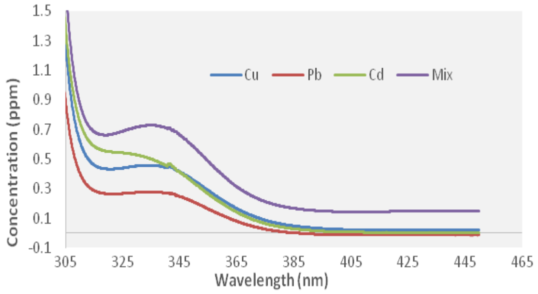

Figure 11: Absorption spectra of 0.2 ppm Cu^{2+}, 0.3 ppm Pb^{2+} and 0.5 ppm Cd^{2+} complexes and their mixture in 0.1 M HCL.

Applying PCR chemometric method

Spectrum values of the measurement set prepared for PCR measurement were read in the wavelength range of 305–445 nm at $\Delta\lambda$=5.0 nm intervals. Variance-covariance matrices of absorbance and concentration values of the measurement set were calculated according to the PCR algorithm. After this calculation, PCR calibration was established. The quantification of the mixed substances was analyzed by reading the absorbance values of the mixtures containing the complexes between 305-445 nm wavelengths. For the validation of the PCR method, 15 mixture solutions were prepared with Pb^{+2}-APDC, Cu^{+2}-APDC, Cd^{+2}-APDC in the working range of 0.25-0.5 µg/mL (Table 6). PCR calibration was performed using this validation set prepared with the values found. Thus, precision and accuracy were tested and recovery (RR) values were calculated. The results obtained by applying the PCR method to synthetic mixtures are Table 2 was also shown.

RSD* Relative Standard Deviation

Validation of Chemometric Method

Cross-validation is a frequently used method for factor selection in establishing PCR calibration[25]. For this purpose, the prediction error sum of squares → PRESS is calculated. The recommended criteria to find the optimal number of factors are PRESS value and F-statistic. The formula given below was used for the calculated PRESS values.

$$\text{PRESS} = \sum_{i=1}^{n}(C_i^{added} - C_i^{found})^2$$

For the validation of chemometric calibrations, the standard error of calibration → SEC parameter is used in the calibration and determination steps. Calibration conditions and F-statistics that minimize the SEC value are used. The following formula was used for the SEC values calculated in the study.

$$\text{SEC} = \sqrt{\frac{\sum_{i=1}^{n}(C_i^{added} - C_i^{found})^2}{n-1}}$$

Here, n is the total number of artificial mixtures. The closeness of the numerical values found to zero is a sign of the accuracy of the applied method[26]. Validation estimation and statistical data regarding PCR calibration are shown in Table 3.

ANOVA test was applied to the data obtained in order to verify the accuracy and precision of the PCR calibration method. In the ANOVA test, it was found that there was no significant difference between the results obtained within the 95% confidence interval, since F-calculated< F-table and *p*-value>*p*=0.05. Two degrees of freedom are used in variance analysis. Degree of freedom between groups=1 Degree of freedom within group = 29.

Since F-calculated< F-table and *p* value>*p*=0.05, it was decided that this calibration model could be used in examining natural water samples.

Table 1: Data of metal complex.

Metal complex	Maximum absorbance	Calibration equation	Correlation coefficient
Pb^{2+}-APDC	339.3 nm	y=0.0355x+0.1933	0.9763
Cu^{2+}-APDC	346.2 nm	y=0.1492x-0.0694	0.9926
Cd^{2+}-APDC	344.5 nm	y=0.053x+0.2774	0.9870

Table 2: Results obtained forPb, Cu and Cd in different synthetic mixtures by using PCR method.

Mix			Found			Recovery		
Pb	**Cu**	**Cd**	**Pb**	**Cu**	**Cd**	**Pb**	**Cu**	**Cd**
0.25	0.1	0.6	0.2476	0.1033	0.6444	99.0703	103.3517	107.4109
0.25	0.2	0.6	0.2512	0.2010	0.6454	100.5103	100.5004	107.5802
0.25	0.3	0.6	0.2458	0.2921	0.6026	98.3367	97.3823	100.4487
0.25	0.4	0.6	0.2560	0.3935	0.5444	102.4008	98.3996	90.7456
0.25	0.5	0.6	0.2404	0.4908	0.6387	96.1612	98.1782	106.4517
0.25	0.25	0.1	0.2546	0.2510	0.1030	101.8508	100.4000	103.0000
0.25	0.25	0.3	0.2436	0.2458	0.2924	97.4544	98.7555	97.4668
0.25	0.25	0.5	0.2468	0.2506	0.4802	98.7507	100.2481	96.0493
0.25	0.25	0.7	0.2442	0.2620	0.6720	97.6984	104.8000	96.0047
0.25	0.25	0.9	0.2586	0.2463	0.8837	103.4558	98.5338	98.1969
0.1	0.25	0.6	0.0967	0.2499	0.6018	96.7034	99.9863	100.3000
0.2	0.25	0.6	0.1964	0.2471	0.5943	98.2400	98.8629	99.0600
0.3	0.25	0.6	0.2970	0.2508	0.6000	99.0175	100.3538	99.9999
0.4	0.25	0.6	0.3941	0.2503	0.5766	98.5350	100.1467	96.1075
0.5	0.25	0.6	0.4979	0.2432	0.5938	99.5828	97.3042	98.9667
			Mean			99.1845	99.8135	99.8526
			RSD*			2.0766	2.0591	4.6824

Application of the developed method on natural water sample

The chemometric method, which was developed in the study and showed high recovery in the calibration and validation stages, was applied to Isparta city water and Süleyman Demirel University campus water.

Table 3: Statistical parameters in the validation-prediction.

Parameter	Pb	Cu	Cd
PRESS	0.0004	0.0004	0.0107
SEC	0.0051	0.0052	0.0026
r	0.9968	0.9975	0.9754
Intercept	0.9963	0.9645	0.9867
Slope	0.0009	0.0081	0.0058

The analyzed water samples were read on a UV spectrophotometer under optimum conditions provided for complex formation. The resulting graphics are Figure 12 and shown in Figure 13. The recovery values found are shown in Table 4.

World Health Organization (WHO) (Cd^{2+} 3 ppm Cu^{+2} 2 ppm and Pb^{2+} 10 ppm), Turkish standards 266 (Cd^{2+} 5 ppm Cu^{+2} 2 ppm and Pb^{2+} 10 ppm) and Ministry of Health (Cd^{2+} 5 ppm Cu^{+2} 2 ppm and Pb^{2+} 10 ppm), the values we obtained as a result of the analysis are well below these values. These results show us the reliability of Isparta province and Süleyman Demirel University campus waters.

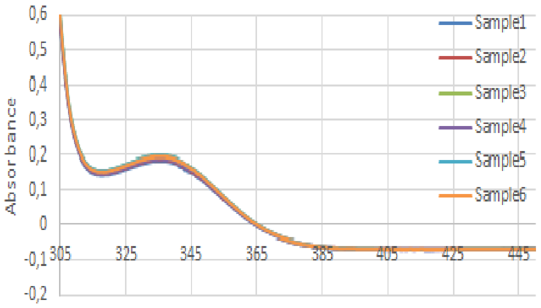

Figure 12: Absorption spectrum of natural water sample taken from Isparta city center (in 0.1 M HCL).

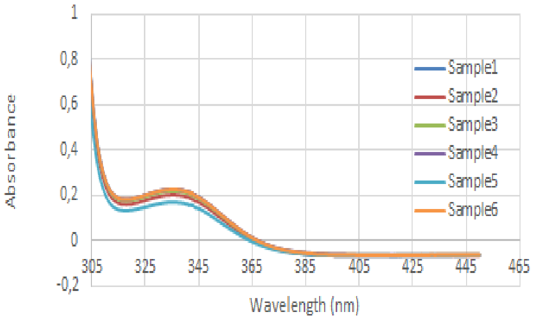

Figure 13: Absorption spectrum of natural water sample taken from Süleyman Demirel University campus (in 0.1 M HCL).

As a result of this study, it was observed that the applied chemometric method gave appropriate results in the analysis of Cd^{2+}, Cu^{2+} and Pb^{2+} mixtures and that the applied methods gave sensitive and accurate results.

Table 4: Recovery values in natural water samples.

Source	Pb	Cu	Cd
Isparta city water	2.8308	0.0074	0.0542
Süleyman Demirel University campus water	2.5785	0.0063	0.0536

Limitations of the study

The limitations of the study were as follows. The water samples analyzed in the study were provided from the interior of Isparta province and from the Campus of Süleyman Demirel University. There are no samples taken from anywhere other than this.

CONCLUSIONS

In this study, a simultaneous spectrophotometric method was proposed by creating complexes of three possible heavy metals caused by the environment and natural resources with APDC ligand in natural water samples. The principal component regression chemometric method was successfully applied to the data obtained as a result of the proposed method. It has been determined that the proposed method gives accurate and sensitive results in determining heavy metals that give absorbance in very close proximity to each other. It was concluded that the proposed method is highly applicable for routine analysis in the determination of heavy metals in natural waters, without requiring any preliminary separation process.

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AUTHOR’S CONTRIBUTION

Aktaş AH: planned the experiments and carried out the writing process. **Gençer İ:** contributed to the study by conducting experiments in laboratory conditions. Both authors revised the article and approved the final version.

DATA AVAILABILITY

The data supporting the findings of this study are not currently available in a public repository but can be made available upon request to the corresponding author. Both authors revised the article and approved the final version.

CONFLICT OF INTEREST

None to declare.

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