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RAPID, HIGHLY SENSITIVE AND SELECTIVE SPECTROPHOTOMETRIC DETERMINATION OF CADMIUM(II) AS AN ION ASSOCIATE OF TETRAIODOCADMIATE(II) WITH ASTRA PHLOXINE

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Abstract

A very simple, rapid, highly sensitive and selective non-extractive spectrophotometric method for the determination of trace amounts of cadmium(II) has been proposed. It is based on the formation of ion association complex (IA) between iodide complex of cadmium Cd(II) [CdJ_4^{2-}] and polymethine dye Astra Phloxine FF. The color of the solution changes from red to red-purple. The color of the IA develops completely at temperature less than 18 °C after 5–10 minutes after mixing of reagents and remains constant for several hours. Opitmal concentrations of HCl, AP and KJ are 0.07–0.13 M, 1.2×10^{-5} M and 6×10^{-3} M, respectively. The molar absorptivity of the IA is 6.5×10^4 mol^{-1} L cm^{-1}. The calibration graph is linear between 1×10^{-7} and 3×10^{-6} mol L^{-1} of cadmium (II). The limit of detection is 5×10^{-8} mol L^{-1} (l = 5 cm, 0.006 mg L^{-1}). A large excess of over 50 cations, anions and some common complexing agents do not interfere with the determination. The method was successfully applied in the determination of cadmium in Wood`s alloy and mine water.

Key words: cadmium determination; ion associate; Astra Phloxine; spectrophotometry; Wood`s alloy; mine water

ЕКСПРЕСНЕ, ВИСОКОЧУТЛИВЕ ТА СЕЛЕКТИВНЕ СПЕКТРОФОТОМЕТРИЧНЕ ВИЗНАЧЕННЯ КАДМІЮ(II) З ВИКОРИСТАННЯМ ІОННОГО АСОЦІАТУ ТЕТРАЙОДОКАДМІАТУ(II) З АСТРАФЛОКСИНОМ

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Анотація

Запропонований дуже простий, швидкий, високочутливий та селективний безекстракційний спектрофотометричний метод для визначення слідових кількостей кадмію(II). Він ґрунтується на утворенні іонного асоціату (ІА) між йодидним комплексом кадмію Cd(II) [CdJ_4^{2-}] та поліметиновим барвником астрафлоксином (АФ). Колір розчину змінюється з червоного на червоно-фіолетовий. Колір ІА повністю розвивається при температурі менше 18 °С через 5–10 хвилин після змішування реагентів і залишається постійним протягом декількох годин. Оптимальні концентрації HCl, АФ та KJ становлять 0.07–0.13 М, 1.2×10^{-5} М та 6×10^{-3} М відповідно. Молярний коефіцієнт світлопоглинання ІА становить 6.5×10^4 моль$^{-1}$ л см$^{-1}$. Градуювальний графік лінійний у межах від 1×10^{-7} до 3×10^{-6} М кадмію(II). Межа виявлення – 5×10^{-8} М (l = 5 см, 0.006 мг л$^{-1}$). Великий надлишок понад 50 катіонів, аніонів та деяких поширених комплексоутворювачів не заважає визначенню. Метод успішно застосований для визначення кадмію у сплаві Вуда та шахтній воді.

Ключові слова: визначення кадмію; іонний асоціат; астрафлоксин; спектрофотометрія; сплав Вуда; шахтна вода.

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ЭКСПРЕССНОЕ, ВЫСОКОЧУВСТВИТЕЛЬНОЕ И СЕЛЕКТИВНОЕ СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ КАДМИЯ(II) С ИСПОЛЬЗОВАНИЕМ ИОННОГО АССОЦИАТА ТЕТРАЙОДОКАДМИАТА(II) С АСТРАФЛОКСИНОМ

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Аннотация

Предложен очень простой, быстрый, высокочувствительный и селективный безэкстракционный спектрофотометрический метод для определения следовых количеств кадмия(II). Он основан на образовании ионного ассоциата (ИА) между йодидным комплексом кадмия Cd(II) $[CdJ_4^{2-}]$ и полиметиновым красителем астрафлоксином (АФ). Цвет раствора меняется с красного на красно-фиолетовый. Цвет ИА полностью развивается при температуре менее 18 °С через 5–10 минут после смешивания реагентов и остается постоянным в течение нескольких часов. Оптимальные концентрации HCl, АФ и KJ составляют 0.07–0.13 М, 1.2×10^{-5} М и 6×10^{-3} М соответственно. Молярный коэффициент светопоглощения ИА составляет 6.5×10^{4} моль$^{-1}$ л см$^{-1}$. Градуировочный график линеен в пределах от 1×10^{-7} до 3×10^{-6} М кадмия(II). Предел обнаружения – 5×10^{-8} М (l = 5 см, 0.006 мг л$^{-1}$). Большой избыток более 50 катионов, анионов и некоторых распространенных комплексообразователей не мешает определению. Метод успешно применен для определения кадмия в сплаве Вуда и шахтной воде.

Ключевые слова: определение кадмия; ионный ассоциат; астрафлоксин; спектрофотометрия; сплав Вуда; шахтная вода.

Introduction

Cadmium is a highly toxic heavy metal occurring naturally in the environment. It enters the biosphere both from natural sources and as a result of human activity. Compared to other heavy metals, cadmium and its compounds are relatively water-soluble. As a result, they are mobile in soil, as a rule more bioavailable and tend to accumulate in biological organisms, including the human body [1]. Cadmium can harm human organs, such as the liver, lungs, and kidneys [2].

Concentrations of cadmium in natural water, drinking water and groundwater are usually less than 1 µg L^{-1} [3]. The World Health Organization and the Environmental Protection Agency have limited the level of cadmium in drinking water to 3.0 µg L^{-1} and 5.0 µg L^{-1}, respectively [4]. A direct spectrophotometric determination of trace Cd(II) in environmental water samples is difficult or impossible due to various factors, in particular, low concentrations and matrix effects [5]. Numerous mine plants produce large quantities of wastewaters containing many toxic elements, including cadmium, in Krivoy Rog region. The typical content of cadmium in such waters is from 1 to 100 µg L^{-1}, i.e. often higher than the permissible concentration. It is necessary to have a sensitive and simple method for the determination of cadmium in mine waters, which can be used in laboratories where there are no instruments for atomic spectroscopy, or in the case when cadmium must be determined immediately after sampling.

Many analytical methods based on molecular (spectrophotometry, luminescence) and atomic spectroscopy (flame and electro thermal atomic absorption spectroscopy [2; 6–8], ICP-AES [9] and X-ray fluorescence [10] techniques) are used to determine cadmium. These atomic spectroscopy methods are sensitive and rapid, but they have some disadvantages, such as time-consuming chemical manipulations, expensive tools, and complicated procedures before processing the sample. Spectrophotometric procedures are still being developed for cadmium determination [11; 12]. Particular attention is drawn to automated flow methods [13; 1], because they are simpler and more economical than other methods. However, most of these methods suffer from certain limitations, such as the interference from a large number of ions, low sensitivity and the need for extraction into organic solvents or the addition of a surfactant. Recently, green analytical chemistry, which relates to the use of environmentally friendly chemicals, has been of great interest [14].

Ion association complexes are often used in chemical analysis, because they allow to achieve the maximum possible sensitivity of spectrophotometric analysis. Extraction is commonly used to separate excess of dye. Non-extractive methods based on a color change that occurs during the formation of IA have been proposed recently [15]. We believe that this color change is associated with the aggregation of dye cations, which occurs more easily due to the approximation of dye cations in slightly soluble crystals of IA. Among others dyes, polymethine dyes differ in their intensive color and resistance of the positively charged form to protonation over a wide pH range. Astra Phloxine (AP) has one of the highest molar absorptivities and is resistant to oxidation. It has already been used in several studies to develop spectrophotometric procedures [16; 17].

Thus, there is a need to develop a new method, which would overcome existing shortcomings in the determination of cadmium(II). The aim of our work was to develop a simple, rapid, sensitive, and selective non-extractive spectrophotometric method for the routine determination of Cd(II) in mine waters. A detailed description of the conditions for the formation of IA is given.

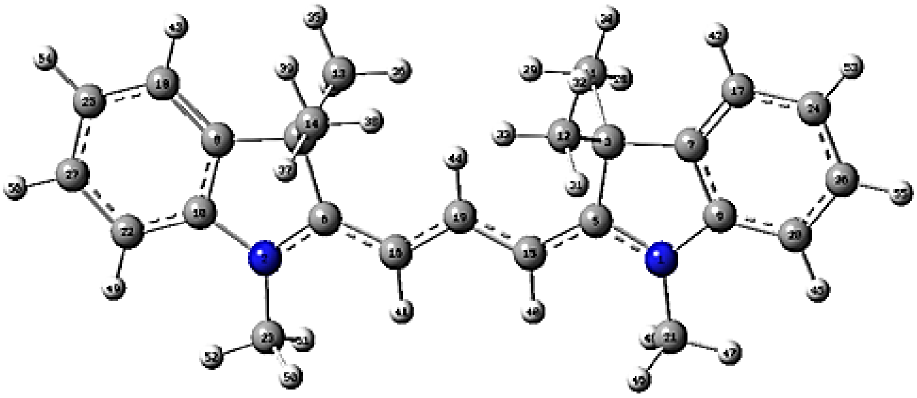


Fig. 1. Structure of Astra Phloxine

Experimental part

Reagents and apparatus. All chemicals used were of analytical-reagent grade of the highest purity available. Double distilled water was used throughout the experiment. A working solution of Cd(II) having a concentration of 10^{-5} mol L^{-1} was prepared by appropriate stepwise dilution of 10^{-3} mol L^{-1} stock solution (0.03085 g of $Cd(NO_3)_2 \times 4H_2O$ was dissolved in 100 mL of distilled water). 1 mol L^{-1} iodide solution was prepared by dissolving 16.6 g of potassium iodide in water and diluting to the mark in a 100 mL volumetric flask. 1 mol L^{-1} hydrochloric acid was prepared by diluting concentrated hydrochloric acid and standardized by titration with NaOH. Astra Phloxine (Basic Red 12, 1, 3, 3-trimethyl-2-[3-(1,3,3-trimethyl-2 indolinylidene)propenyl]-3H-indolium chloride) was purchased from Hangzhou Dayangchem Co., Ltd. (China) and used without purification. 1 mmol L^{-1} Astra Phloxine stock solution was prepared by dissolving 0.444 g of AP in 10 mL of ethanol and diluting to 1000 mL with purified water. Spectrophotometric measurements were made with the UV-VIS spectrophotometer SF-46 (LOMO, Russia) using glass cells with a pathlength of a 50 mm.

Calibration curve construction. The amount of sample corresponding to a final concentration of cadmium in the range from 2×10^{-7} to 3×10^{-6} mol L^{-1} was placed in a 25 mL volumetric flask. Then 2.5 mL of 1 mol L^{-1} HCl, 1,5 mL of 1 mol L^{-1} KI and 3 mL of 1×10^{-4} mol L^{-1} AP solution were sequentially added. The solution of dye should be added by small portions with vigorous shaking after each addition. Finally, the volume was diluted to the mark with distilled water, the solution was thoroughly mixed. The absorbance of the complex was measured at 600 nm against water. The glass cuvettes must be periodically cleaned with concentrated nitric acid to remove the residues of IA precipitate on the cell walls.

Determination of cadmium(II) in mine waters. Samples of mine water (250 – 1000 mL) are filtered (several times, if necessary) using Whatman filter № 40, evaporated to almost dryness, the inner walls of the flask are washed with a small volume of water and evaporated many times. Then the residue is quantitatively transferred to filter paper. The filter is washed with 10 mL of hot distilled water to dissolve the salts. The resulting solution is collected in a 25 mL calibration flask and further the analysis is carried out as described above. To eliminate the interfering effect of some metal ions, 1 mL of 0.05 M EDTA, or 1 mL of 1 % ascorbic acid was added as masking agent.

Analysis of cadmium alloys. A mass of an alloy sample (Wood or Rose alloy) of is taken in a beaker, 15 mL of concentrated hydrochloric acid and 5 mL of concentrated nitric acid are added. The sample is completely dissolved by heating on a hot plate. If necessary 10 ml of concentrated hydrochloric acid are added to complete dissolution. The resulting solution is filtered through a Whatman № 40 filter paper into a 100 mL calibrated flask. The residue is washed with a small volume of water, and the volume is made up with distilled water. A suitable aliquot (1–5 mL) of the above solution is taken into a 25 mL calibrated flask and the cadmium content is determined using the procedure described above using 3-methyl-2,6-dimercapto-1,4-thiopyrone as a masking agent.

Results and discussion

The color reaction between tetraiodocadmiate and Astra Phloxine. The color change in the reaction between some anions and cationic dyes occurs only under specially developed experimental conditions [15–18]. The prerequisites for the formation of a specific IA are a reasonably high size of counterions and low solubility of the resulting IA. As an analytical form for the determination of cadmium(II), IA, formed between a large tetraiodocadmiate anion and a polymethine dye Astra Phloxine, was chosen. It was found that a precipitate is easily formed after mixing concentrated solutions of the above ions. The color of solution, as well as the precipitate, markedly differs from the primary color of the dye and changes from red to red-violet. However, when the concentration of the complex anion is lower than 3×10^{-6} mol L^{-1}, the resulting solution containing finely dispersed particles of IA is stable for a long time. The stability of a finely dispersed solution of IA depends on its concentration.

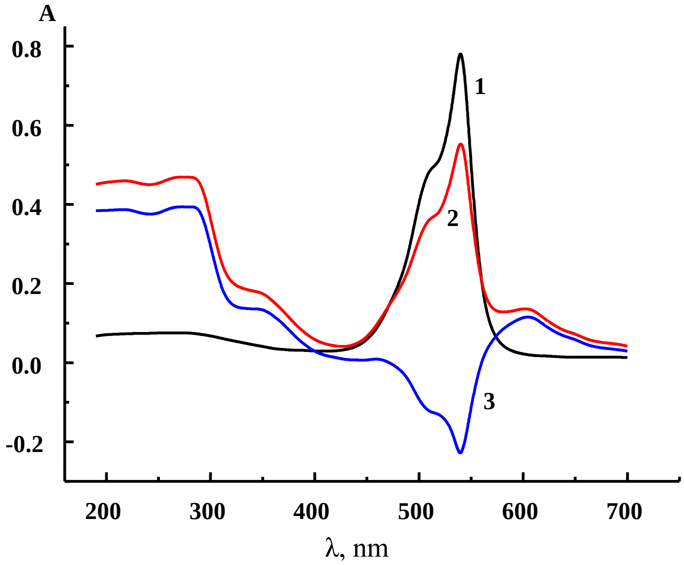


Fig. 2. Absorption spectra of AP^+ (1), IA $AP_2[CdI_4]$ (2), and ΔA (3)

The electronic spectrum of the singly charged AP^+ cation in aqueous solution is characterized by an intensive absorption band with a maximum at 542 nm. Formation of IA leads to two important changes in the UV-visible spectrum of AP^+. It expands significantly and a shoulder or band appears at about 600 nm (Fig. 2). We have chosen this wavelength as analytical. It is also important that the dye absorbance in this spectral region is low and less than 0.01.

Optimization of formation conditions of IA.

Effect of acidity. It was established that several factors have a significant influence on the absorbance of IA, including acidity, concentration of dye and iodide ions, temperature and time of reaction. The nature and concentration of the acid are especially important, since complex anion is stable only in a comparatively narrow range of acidity and, in addition, the simultaneous reaction with anions of acid should be taken into account. The effect of nitric, sulfuric, hydrochloric and phosphoric acid was studied. Hydrochloric acid was found to be the most suitable. A wider range of optimal acidity and higher absorbance were found when hydrochloric acid was used for acidification. Absorbance of specific IA was maximal and constant in the range of HCl concentrations from 0.07 to 0.13 M. Absorbance decreases outside this range of acidity (Fig. 3).

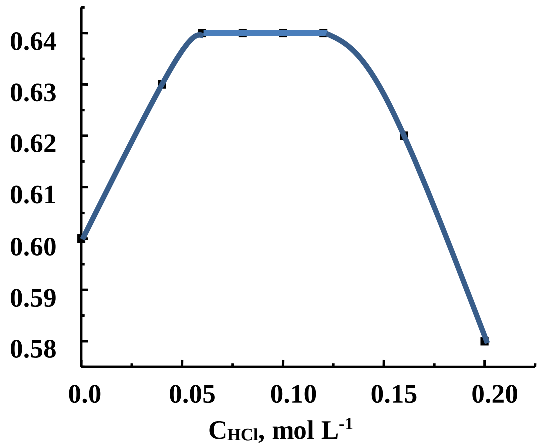


Fig. 3. Effect of the acidity on the absorbance of IA AP$_2$[CdI$_4$]. $C_{Cd} = 2\times10^{-6}$ M, $C_{KJ} = 0.1$ M, $C_{AP} = 1.4\times10^{-5}$ M, λ = 600 nm, l = 5 cm

Effect of iodide concentration on the formation and absorbance of complex. The effect of potassium iodide concentration on the formation of the ion association complex in an aqueous solution was studied. The concentration of KI ranged from 0.01 to 0.12 M. The constant and maximum absorbance of the complex was observed when the concentration of iodide in the aqueous solution exceeded 0.05 M (Fig. 4). For further work, 6×10^{-3} M potassium iodide was used. Even with a large excess of iodide ions, the absorbance does not grow, which indicates the formation of a saturated complex with the composition of CdI$_4^{2-}$.

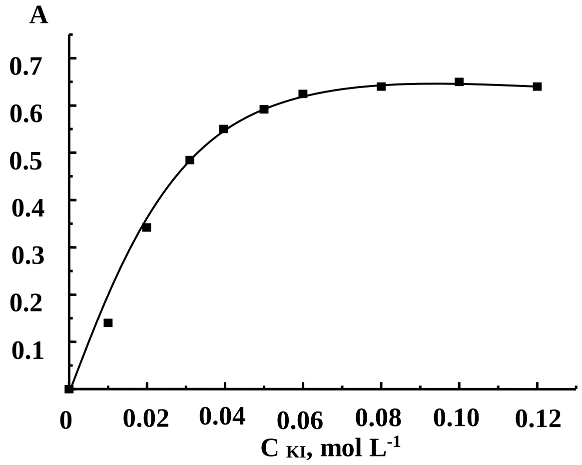


Fig. 4. Effect of the KI concentration on the absorbance of IA AP$_2$[CdI$_4$].$C_{Cd(II)} = 2\times10^{-6}$ M, $C_{HCl} = 0.1$ M, $C_{AP} = 1.4\times10^{-5}$ M, λ = 600 nm, l = 5 cm

Effect of Astra Phloxine concentration on the absorbance of IA. The effect of concentration of Astra Phloxine on the color development of the IA complex was studied. Absorbance of IA increases to 1.2×10^{-5} M and then levels off (Fig. 4). This concentration was used in further experiments. The inflection point on the saturation curve does not correspond to composition of IA, i.e. IA can be assigned to complexes with medium stability. However, in comparison with the case of the formation of IA with singly charged anions, the optimal concentration is much bigger.

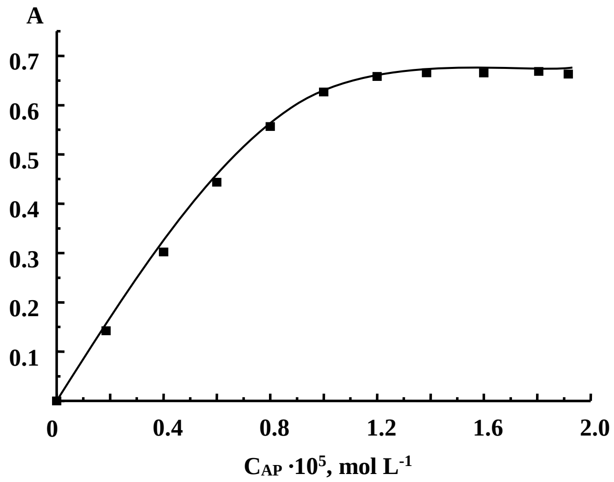
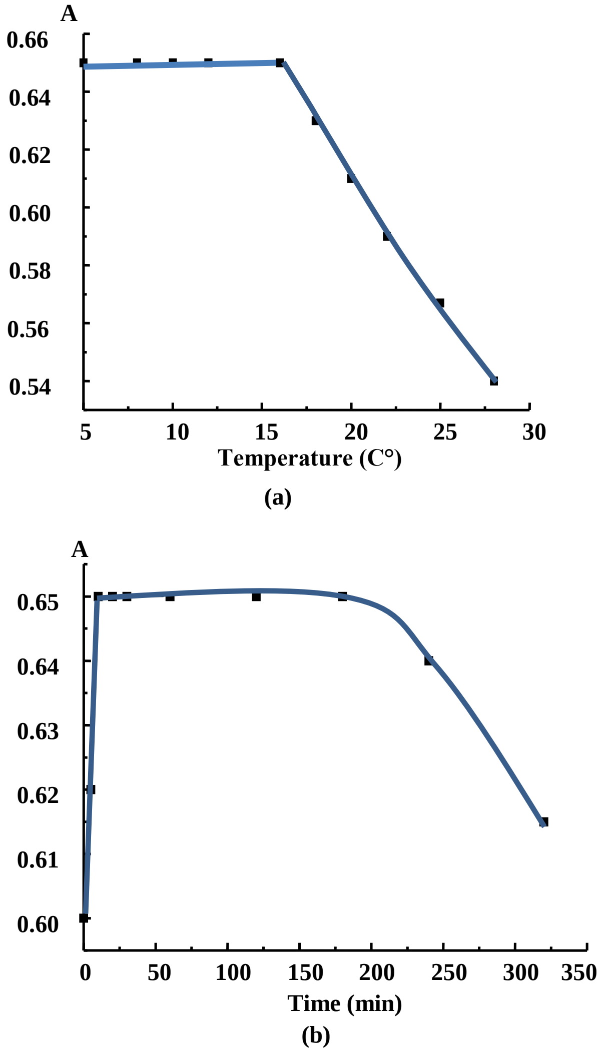


Fig. 5. Effect of the AP concentration on the absorbance of IA AP$_2$[CdI$_4$]. $C_{Cd} = 2\times10^{-6}$ M, $C_{HCl} = 0.1$ M, $C_{KJ} = 0.1$ M, λ = 600 nm, l = 5 cm

IA of the singly charged [BiI$_4^-$] anion with AP$^+$ is completely formed, starting from 1.2×10^{-5} M.

Effect of time and temperature. The behavior of cadmium IA in time differs from this for other studied specific IAs. Typically, specific IAs are formed instantly. In the example studied in this work, most of the color appears very quickly, but complete absorbance develops within about 5-10 minutes depending on the temperature (Fig. 6a). After that, the absorbance remains constant for at least 4 hours.

In this work, it was shown for the first time that the temperature of a solution substantially affects the stability and absorbance of the formed specific IA. The influence of temperature on the formation of IA was studied in the range from 5 to 30 °C. It was found that the absorbance of the solution decreases markedly and does not reach its maximum value if the temperature of the solution is above 18 °C. At a higher temperature, the IA precipitate dissolves, causing the dye aggregates to disaggregate, that results in the absorbance decrease. Therefore, we recommend coolling distilled water, all reagents and sample solutions before starting the experiment.



(a)

(b)

Fig. 6. Effect of temperature (a) and time (b) on the absorbance of IA $AP_2[CdI_4]$

Reaction chemistry and composition of the specific ion association complex. The change in the solution color is associated with the formation of a specific ion association complex between AP cations and anions of the iodide complex of cadmium (II). The reaction chemistry involves the formation of iodide complexes in the first stage, which may have stoichiometry for Cd^{2+} : I^- as 1 : 3 or 1 : 4. The inflection point on the continuous variation curve does not correspond to the correct stoichiometry of the complex when saturated with iodide or dye. Therefore, the composition of the complex was examined by Job's method. It can be seen from Fig. 7 that the maximum on the curve is approximately situated at a molar ratio of dye to complex anion of 0.67 : 0.33 or 2 : 1. Hence, there are two AP cations in the molecule of IA, and formula of IA should be written as $AP_2[CdI_4]$.

The composition of IA was confirmed by chemical analysis of a slightly soluble salt precipitated from a concentrated solution of IA. 10 mL of 10^{-4} M Cd^{2+} were mixed with 5 mL of 1 M KI. After that, an excess of dye was added (15 mL of 10^{-5} M). The precipitate was filtered, washed with distilled water and air-dried. The content of the dye was determined after dissolving in a certain volume of dimethylformamide. We calculated the values of molar absorptivity coefficients for two possible compositions of IA and compared with the theoretical one. For the IA with a composition of Rhodamine 6G to CdI_4^{2-} = 2:1, the theoretical molar absorptivity should be 105000, and the experimentally found value was almost the same and equal to 102000. The same composition for IA was proposed in [1].

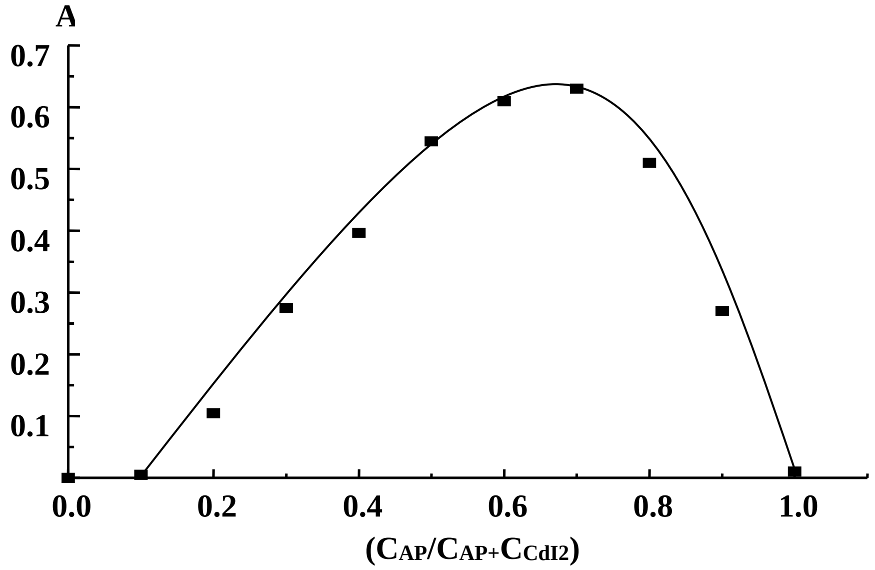


Fig. 7. Determination of composition of IA using continuous variation method

The contrast change in the color of the IA is well explained by the theory of excitons [15]. The approach of dye ions occurs naturally when a precipitate is formed between the dye cations and the anions of iodide complex of cadmium(II). The conditions are created for the π-π interaction of aromatic systems of the dye molecules. In this way, formation of dimers of more highly ordered dye aggregates is promoted. The result of exciton splitting of excited states in the aggregated dye is a strong spectral shift of the absorption band. The formation of extremely poorly soluble particles of basic dyes with HPAs is of great importance in stimulating dye aggregation.

Calibration Graph (Beer's Law and Sensitivity). Under the optimal conditions found for the formation reaction of IA $AP_2[CdJ_4]$, the calibration curve was linear from 1×10^{-7} to 3×10^{-6} mol L^{-1} of Cd(II). The equation of the calibration graph was $A = (0.325\pm0.004) \times C_{Cd(II)}$, and the correlation coefficient was 0.9990. The detection limit of the present method was 5×10^{-8} M. The molar absorptivity of the complex with respect to Cd(II) was 6.5×10^{4} mol^{-1} L cm^{-1} at 600 nm. The value of the molar absorptivity or the slope of calibration graph can be perfectly reproduced if the determination is carried out under the conditions recommended in section 2.2.

Interference study. The selectivity of the proposed method was examined by adding various concentrations of interfering ions in a Cd(II) solution containing 2×10^{-6} mol L^{-1} of metal ion. Tolerance limits of various ions are summarized in Table 1. It was noted that most ions do not have influence on the determination of Cd(II). Alkaline, alkaline earth, Al(III), most transition metal ions do not interfere with the determination of Cd(II) with a large excess. Hg(II), Bi(III), Pd(II), Ag(I) and other metals of the platinum group ions cannot be tolerated. It was found that preliminary precipitation with 3-methyl-2,6-dimercapto-1,4-thiopyrone [19-21] can be used to separate these ions completely. The results show that the proposed method is highly selective.

Table 1

Tolerance limits for the determination of 2×10^{-6} mol L^{-1} of Cd(II) with the developed method

Ion tested	Tolerance limit, mol L^{-1}
Na^+, K^+, NH_4^+, NO_3^-, SO_3^{2-}	0.1
Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Be^{2+}	0.1
Br^-	0.01
Ni(II), Co(II), Mn(II), Cr(II)	0.01
Al(III), Fe(II), Fe(III)	0.001
As(V), Se(IV)	0.001
Cu(II), Zn(II)	4×10^{-4}
Zr(IV), Ta(V)	1×10^{-4}
Mo(VI)	2×10^{-3}
W(VI)	5×10^{-5}
Pd(II)	5×10^{-7}
Pt(IV)	5×10^{-5}
Ag(I), Hg(II)	5×10^{-7}
Pb(II), Bi(III)	1×10^{-6}
Sodium dodecylbenzenesulfonate	2×10^{-6}
Citric acid	0.01
Triton X-100	0.01
EDTA	1×10^{-6}
Thiourea	5×10^{-3}

Analysis of real samples. The proposed method was successfully applied for the analysis of Cd(II) in environmental water samples, such as mine and drinking water. Most spectrophotometric methods for the determination of cadmium in natural and marine waters require preliminary concentration of cadmium [14]. The concentration of cadmium in natural and sea water is a few µg L^{-1}. The concentration of cadmium found in U.S. drinking water is from 0.4 to 60 µg L^{-1} [22]. The results of the analysis of mine water were in excellent agreement with the results obtained using atomic absorption spectroscopy (Table 2). The content of cadmium was determined in Certified Reference Material.

Table 2

Content of cadmium in samples of mine water of Krivoy Rog district

Sample	C(Cd), ppm AAS method	C(Cd), ppm Proposed method	Found, %*	RSD, %**
18	0.0100	0.0112 ± 0.0024	112	2.4
5	0.0090	0.0093 ± 0.0006	103	4.2
7	0.0080	0.0084 ± 0.0014	104	1.7

* Found: C(Cd) found by proposed method/C(Cd) found by AAS method×100%

** RSD Relative standard deviation

Wood alloy contained 12.5% Sn, 25% Pb, 50 % Bi, and 12.5 % Cd. It was found ($P = 0.95$, $n = 5$) 12.69 ± 0.33 with $S_r = 0.021$. Interfering effect of Bi(III) was eliminated by preliminary adding 2 mL of 10^{-4} M 3-methyl-2,6-dimercapto-1,4-thiopyrone solution to the aliquot of analyzed sample and filtrating the resulting precipitate.

Comparison of methods. The characteristics of the method were compared with similar published spectrophotometric data for the determination of Cd(II). A comparison of the sensitivity of various reagents is given in Table 3. It also shows that the proposed method is simple, rapid and selective. The method does not require heating, aging or extracting with organic solvents.

Table 3

Comparison of the sensitivity of the methods for the spectrophotometric determination of cadmium(II)

Molar absorptivity, mol^{-1} L cm^{-1}	Linearity range, mg L^{-1}	λ_{max}, nm	Limit of detection, mg L^{-1}	Reference
2.94×10^4	0.50 – 5.05	378	0.5035	12
5.2×10^4	3 – 44	600	0.96	22
6.1×10^4	0.04 – 2	685	0.04	23
4.03×10^3	5.62 – 16.86	440	28	24
1.75×10^4	0.5 – 4.0	550	0.2	25
2.5×10^5	0.42 – 9.2	510	4.5	26
2.05×10^4	0.5 – 6.0	630-640	0.13	27
5.3×10^3	0.1 – 30	396	0.1	28
6.5×10^4	0.011 – 0.34	600	0.006	Present work

Conclusions

A new simple, sensitive, selective and inexpensive non-extractive spectrophotometric method for the determination of cadmium(II) has been developed. The method is based on the formation of the ion association complex between the anionic iodide complex of cadmium(II) and polymethine dye Astra Phloxine as a color reagent. The detection limit of the present method is 5×10^{-8} M. It was found that the molar absorptivity of the ion associate is 6.5×10^4 mol^{-1} L cm^{-1} at 600 nm.

The proposed method has several important advantages. It does not include extraction separation of excess dye. This eliminates the use of organic solvents, and this method can be considered as «green analytical procedure». Reagents used are available and inexpensive. Excessive amount of reagent in the sample solution does not interfere with determination, which is a significant advantage in comparison with other groups of reagents. The most common ions do not interfere with the determination and, when dimercaptothiopyrone is used, the proposed method can be considered as specific for cadmium(II) ions. The proposed method is more selective than other procedures recommended in the literature, requiring the use of masking agents only in exceptional cases.

The simplicity of the method allows its use for the routine determination of cadmium(II) in a variety of samples. The proposed method was successfully applied for the analysis of Cd(II) in different samples such as mine, drinking waters and alloys. The results of the analysis of mine water by the spectrophotometric method were in excellent agreement with the results obtained using AAS. There was no significant difference between the certified cadmium content and the one found by analyzing the certified reference material. Considering the high sensitivity, selectivity, and reproducibility of the proposed methodology, it can be recommended as an arbitration procedure. Another important feature of the method is that it can be easily automated.

Бібліографічні посилання

[1] Škrlíková J. A novel non-extractive sequential injection procedure for determination of cadmium / J. Škrlíková,

V. Andruch, H. Sklenářová [et al.] // Anal. Lett. – 2011. – Vol. 44, № 1–3. – P. 431–445.

[2] da Silva J. B. B. Determination of cadmium in biological samples solubilized with tetramethylammonium hydroxide by electrothermal atomic absorption spectrometry, using ruthenium as permanent modifier / J. B. B. da Silva, D. L. G. Borges, M. A. M. S. da Veiga [et al.] // Talanta. – 2003. – Vol. 60, № 5. – P. 977–982.

[3] Shirkhanloo H. Cadmium determination in human biological samples based on trioctylmethyl ammonium thiosalicylate as a task-specific ionic liquid by dispersive liquid–liquid microextraction method / H. Shirkhanloo, M. Ghazaghi, H. Z. Mousavi // J. Molec. Liquids. – 2016. – Vol. 218. – P. 478–483.

[4] Fırat M. Determination of trace amount of cadmium using dispersive liquid-liquid microextraction-slotted quartz tube-flame atomic absorption spectrometry / M. Fırat, S. Bakırdere, M. S. Fındıkoğlu [et al.] // Spectrochim. Acta B. – 2017. – Vol. 129. – P. 37–41.

[5] Gao L. Determination of Cd(II) in water samples by summable spectrophotometry of positive-negative peaks after cloud point extraction / L. Gao, F. Chen, H. Y. Yang [et al.] // Advanced Materials Research. – 2012. – Vol. 573–574. – P. 48–52.

[6] de Castro Maciel C. J. Determination of cadmium in human urine by electrothermal atomic absorption spectrometry / C. J. de Castro Maciel, G. M. Miranda, D. P. de Oliveira // Anal. Chim. Acta. – 2003. – Vol. 491, № 2. – P. 231–237.

[7] Kendüzler E. Determination of trace cadmium in waters by flame atomic absorption spectrophotometry after preconcentration with 1-nitroso-2-naphthol-3, 6-disulfonic acid on Ambersorb 572 / E. Kendüzler, A. R. Türker // Annali di Chimica: Journal of Analytical, Environmental and Cultural Heritage Chemistry. – 2005. – Vol. 95, № 1-2ю – P. 77–85.

[8] Welz B. Flame atomic absorption spectrometric determination of cadmium, cobalt, and nickel in biological samples using a flow injection system with on-line preconcentration by co-precipitation without filtration / B. Welz, S. Xu, M. Sperling // Applied spectroscopy. – 1991. – Vol. 45, № 9. – P. 1433–1443.

[9] Zougagh M. Determination of cadmium in water by ICP-AES with on-line adsorption preconcentration using DPTH-gel and TS-gel microcolumns / M. Zougagh, de A.G. Torres, J.C. Pavon // Talanta. – 2002. – Vol. 56, № 4. – P. 753–761.

[10] Marguí E. Determination of cadmium at ultratrace levels in environmental water samples by means of total reflection X-ray spectrometry after dispersive liquid–liquid microextraction / E. Marguí, I. Queralt, M. Hidalgo // J. Anal. Atomic Spectrometry. – 2013. –Vol. 28, № 2. – P. 266–273.

[11] Watanabe H. Dual-wavelength spectrophotometric determination of cadmium with cadion / H. Watanabe, H. Ohmori // Talanta. – 1979. – Vol. 26, № 10. – P. 959–961.

[12] Nagalaxmi B. N. Determination of trace amount of Cd(II) by using a chromogenic reagent diacetylmonoxime-3-amino-4-hydroxy benzoyl hydrazone (DMAHBH) with UV-visible spectrophotometry / B. N. Nagalaxmi, C. Viswanatha, K. R. Reddy, K. B. Chandrasekhar, N. Donappa // European Reviews of Chemical Research. – 2015. – № 2. – P. 104–111.

[13] Di Nezio M. S. Automated flow-injection method for cadmium determination with pre-concentration and reagent preparation on-line / M. S. Di Nezio, M. E. Palomeque, B.S.F. Band // Química Nova. – 2005. – Vol. 28, № 1. – P. 145–148.

[14] A simple flow injection spectrophotometric procedure for iron (III) determination using Phyllanthus emblica Linn. as a natural reagent / N. Jaikrajang, S. Kruanetr, D.J. Harding, P. Rattanakit // Spectrochim. Acta A. – 2018. – Vol. 204. – P. 726–734.

[15] Vishnikin A. B. Analytical effects based on interaction of organic dyes with heteropoly anions, anionic metal complexes and cationic polyelectrolytes / A. B. Vishnikin, Al- M. E. A. Shwaiyat, S. I. Okovytyy [et al.] // In «Scientific developments and achievements». – London: Sciemcee Publishing, 2018. – P. 181–208.

[16] Rapid, sensitive and selective spectrophotometric determination of phosphate as an ion associate of 12-molybdophosphate with Astra Phloxine / A.B. Vishnikin, M. K. E. A. Al-Shwaiyat, Ya. R. Bazel, V. Andruch // Microchim. Acta. – 2007. – Vol. 159, № 3-4. – P. 371–378.

[17] Liquid–liquid microextraction and spectrophotometric determination of anionic surfactants using Astra Phloxine FF / V. Lavra, Ya. Bazel, M. Badida, V. Andruch // Int. J. Environ. Anal. Chem. – 2015. – Vol. 95, № 3. – P. 217–224.

[18] Vishnikin A. B. Novel indirect spectrophotometric methods for determination of phosphate and arsenate using polyoxometalates and micellar medium / A. B. Vishnikin // J. Molec. Liquids. – 2005. – Vol. 118, № 1-3. – P. 51–55.

[19] Khudyakova S. N. A highly selective and sensitive colorimetric chemosensor based on polyurethane foam impregnated with 3-methyl-2,6-dimercapto-1,4-thiopyrone for on-site preconcentration and determination of palladium(II) / S. N. Khudyakova, A. B. Vishnikin, N. M. Smityuk // Int. J. Environ. Anal. Chem. – 2018. – Vol. 98, № 13. – P. 1253–1273.

[20] Chmilenko F. A. Sorption preconcentration and separation of Palladium(II) and Platinum(IV) for visual test and densitometric determination / F. A. Chmilenko, S. N. Khudyakova // J. Anal. Chem. – 2013. – Vol. 68, № 5. – P. 409–416.

[21] Chmilenko F. A. Sorption-colorimetric and test determination of osmium in alloys and concentrates / F. A. Chmilenko, S. N. Khudyakova // J. Anal. Chem. – 2010. – Vol. 65, № 9. – P. 907–911.

[22] Amin A. S. Spectrophotometric determination of cadmium using thiazolylazo chromogenic reagents in the presence of triton X-100: Application in environmental samples / A. S. Amin / Anal. Lett. – 2001. – Vol. 34, № 1. P. 163–176.

[23] Garcia I. L. Manual and FIA methods for the determination of cadmium with malachite green and iodide / I. L. Garcia, P. Navarro, M. H. Cordoba // Talanta. – 1988. – Vol. 35, № 11. – P. 885–889.

[24] Parikh K. S. New spectrophotometric method for determination of cadmium / K.S. Parikh, R.M. Patel, K.N. Patel // E-Journal Chem. – 2009. – Vol. 6. – S496–S500.

[25] Shar G.A. Spectrophotometric determination of metal complexes of 1-(2 pyridylazo)-2-naphthol in micellar medium / G.A. Shar, M.I. Bhanger / J. Chem. Soc. Pakistan. – 2003. – Vol. 25, № 1. – P. 28–33.

[26] Hashem E.Y. Spectrophotometric studies on the simultaneous determination of cadmium and mercury with 4-(2-pyridylazo)-resorcinol / Hashem E.Y. // Spectrochim. Acta A. – 2002. – Vol. 58, № 7. – P. 1401–1410.

[27] Bulgariu L. Spectrophotometric determination of cadmium(II) using p,p′-dinitro-SYM-diphenylcarbazid

in aqueous solutions / L. Bulgariu, D. Bulgariu, I. Sarghie // Anal. Lett. – 2005. – Vol. 38, № 14. P. 2365–2375.

[28] Ahmed M.J. A simple spectrophotometric method for the determination of cadmium in industrial, environmental, biological and soil samples using 5,7-dibromo-8-hydroxyquinoline / M.J. Ahmed, M.T.I. Chowdhury // Anal. Sci. – 2004. – Vol. 20. – P. 987–990.

References

[1] Škrlíková, J., Andruch, V., Sklenářová, H., Solich, P., Balogh, I. S., Billes, F. (2011). A novel non-extractive sequential injection procedure for determination of cadmium. *Anal. Lett., 44*(1–3), 431–445. https://doi.org/10.1080/00032719.2010.500783

[2] da Silva, J.B.B., Borges, D.L.G., da Veiga, M.A.M.S., Curtius, A.J., Welz, B. (2003). *Talanta*, *60*(5), 977–982. https://doi.org/10.1016/S0039-9140(03)00182-6

[3] Shirkhanloo, H., Ghazaghi, M., Mousavi, H.Z. (2016). Cadmium determination in human biological samples based on trioctylmethyl ammonium thiosalicylate as a task-specific ionic liquid by dispersive liquid–liquid microextraction method. *J. Molec. Liquids*, *218*, 478–483. https://doi.org/10.1016/j.molliq.2016.02.035

[4] Fırat, M., Bakırdere, S., Fındıkoğlu, M. S., Kafa, E. B., Yazıcı, E., Yolcu, M., Turak, F. (2017). Determination of trace amount of cadmium using dispersive liquid-liquid microextraction-slotted quartz tube-flame atomic absorption spectrometry. *Spectrochim. Acta B*, *129*, 37–41. https://doi.org/10.1016/j.sab.2017.01.006

[5] Gao, L., Chen, F., Yang, H.Y., Yan, G.H., Zhong, G.X. (2012). Determination of Cd(II) in water samples by summable spectrophotometry of positive-negative peaks after cloud point extraction. In *Advanced Materials Research, 573–574*, 48–52. https://doi.org/10.4028/www.scientific.net/AMR.573-574.48

[6] de Castro Maciel, C. J., Miranda, G.M., de Oliveira, D.P., de Siqueira, M.E.P., Silveira, J.N., Leite, E.M.A., da Silva, J.B.B. (2003). Determination of cadmium in human urine by electrothermal atomic absorption spectrometry. *Anal. Chim. Acta*, *491* (2), 231–237. https://doi.org/10.1016/S0003-2670(03)00820-1

[7] Kendüzler, E., Türker, A.R. (2005). Determination of trace cadmium in waters by flame atomic absorption spectrophotometry after preconcentration with 1-nitroso-2-naphthol-3, 6-disulfonic acid on Ambersorb 572. *Annali di Chimica: Journal of Analytical, Environmental and Cultural Heritage Chemistry*, *95* (1-2), 77–85. https://doi.org/10.1002/adic.200590009

[8] Welz, B., Xu, S., Sperling, M. (1991). Flame atomic absorption spectrometric determination of cadmium, cobalt, and nickel in biological samples using a flow injection system with on-line preconcentration by co-precipitation without filtration. *Applied spectroscopy*, *45*(9), 1433–1443. https://doi.org/10.1366%2F0003702914335625

[9] Zougagh, M., de Torres A. G., Pavon J. C. (2002). Determination of cadmium in water by ICP-AES with on-line adsorption preconcentration using DPTH-gel and TS-gel microcolumns. *Talanta*, *56* (4), 753–761. https://doi.org/10.1016/S0039-9140(01)00605-1

[10] Marguí, E., Queralt, I., Hidalgo, M. (2013). Determination of cadmium at ultratrace levels in environmental water samples by means of total reflection X-ray spectrometry after dispersive liquid–liquid microextraction. *J. Anal. Atomic Spectrometry*, *28*(2), 266–273. https://doi.org/10.1039/C2JA30252G

[11] Watanabe, H., Ohmori, H. (1979). Dual-wavelength spectrophotometric determination of cadmium with cadion. *Talanta*, *26* (10), 959–961. https://doi.org/10.1016/0039-9140(79)80133-2

[12] Nagalaxmi, B.N., Viswanatha, C., Reddy, K.R., Chandrasekhar, K.B., Donappa, N. (2015). Determination of trace amount of Cd(II) by using a chromogenic reagent diacetylmonoxime-3-amino-4-hydroxy benzoyl hydrazone (DMAHBH) with UV-visible spectrophotometry. *European Reviews of Chemical Research*, (2), 104–111. https://doi.org/10.13187/ercr.2015.4.104

[13] Di Nezio, M. S., Palomeque, M. E., Band, B. S. F. (2005). Automated flow-injection method for cadmium determination with pre-concentration and reagent preparation on-line. *Química Nova*, *28* (1), 145–148. http://dx.doi.org/10.1590/S0100-40422005000100025

[14] Jaikrajang, N., Kruanetr, S., Harding, D. J., Rattanakit, P. (2018). A simple flow injection spectrophotometric procedure for iron (III) determination using Phyllanthus emblica Linn. as a natural reagent. *Spectrochim. Acta A*, *204*, 726–734. https://doi.org/10.1016/j.saa.2018.06.109

[15] Vishnikin, A.B., Al-Shwaiyat, M.E.A., Okovytyy, S.I., Chernavskaya, A.Yu., Hedjazi, M. (2018). Analytical effects based on interaction of organic dyes with heteropoly anions, anionic metal complexes and cationic polyelectrolytes. In *«Scientific developments and achievements»*. London: Sciemcee Publishing, 2018. – P. 181–208.

[16] Vishnikin, A. B., Al-Shwaiyat, M. K. E., Bazel, Ya. R., Andruch, V. (2007). Rapid, sensitive and selective spectrophotometric determination of phosphate as an ion associate of 12-molybdophosphate with Astra Phloxine. *Microchim. Acta*, *159* (3-4), 371–378. https://doi.org/10.1007/s00604-007-0754-7

[17] Lavra, V., Bazel, Y., Badida, M., Andruch, V. (2015). Liquid–liquid microextraction and spectrophotometric determination of anionic surfactants using Astra Phloxine FF. *Int. J. Environ. Anal. Chem.*, *95* (3), 217–224. https://doi.org/10.1080/03067319.2014.1002488

[18] Vishnikin, A.B. (2005). Novel indirect spectrophotometric methods for determination of phosphate and arsenate using polyoxometalates and micellar medium. *J. Molec. Liquids, 118* (1-3), 51–55. https://doi.org/10.1016/j.molliq.2004.07.012

[19] Khudyakova, S. N., Vishnikin, A. B., Smityuk, N. M. (2018). A highly selective and sensitive colorimetric chemosensor based on polyurethane foam impregnated with 3-methyl-2,6-dimercapto-1,4-thiopyrone for on-site preconcentration and determination of palladium(II). *Int. J. Environ. Anal. Chem., 98*(13), 1253–1273. https://doi.org/10.1080/03067319.2018.1544634

[20] Chmilenko, F.A., Khudyakova, S.N. (2013). Sorption preconcentration and separation of Palladium(II) and Platinum(IV) for visual test and densitometric determination. *J. Anal. Chem., 68* (5), 409–416.

[21] Chmilenko, F.A., Khudyakova, S.N. (2010). Sorption-colorimetric and test determination of osmium in alloys and concentrates. *J. Anal. Chem., 65* (9), 907–911. https://doi.org/10.1134/S1061934810090042

[22] Amin, A.S. (2001). Spectrophotometric determination of cadmium using thiazolylazo chromogenic reagents in the presence of triton X-100: Application in environmental samples. *Anal. Lett.*, *34* (1), 163–176. https://doi.org/10.3329/jce.v25i0.7233

[23] Garcia, I. L., Navarro, P., Cordoba, M. H. (1988). Manual and FIA methods for the determination of cadmium with malachite green and iodide. *Talanta*, *35* (11), 885–889. https://doi.org/10.1016/0039-9140(88)80207-8

[24] Parikh, K. S., Patel, R. M., Patel, K. N. (2009). New spectrophotometric method for determination of cadmium. *E-Journal Chem.*, *6*, S496–S500. http://dx.doi.org/10.1155/2009/219736

[25] Shar, G. A., Bhanger, M. I. (2003). Spectrophotometric determination of metal complexes of 1-(2 pyridylazo)-2-naphthol in micellar medium. *J. Chem. Soc. Pakistan*, *25* (1), 28–33.

[26] Hashem, E. Y. (2002). Spectrophotometric studies on the simultaneous determination of cadmium and mercury with 4-(2-pyridylazo)-resorcinol. *Spectrochim. Acta A*, *58* (7), 1401–1410. https://doi.org/10.1016/S1386-1425(01)00590-X

[27] Bulgariu, L., Bulgariu, D., Sarghie, I. (2005). Spectrophotometric determination of cadmium(II) using p,p′-dinitro-SYM-diphenylcarbazid in aqueous solutions. Anal. Lett., 38 (14), 2365–2375. https://doi.org/10.1080/00032710500316597

[28] Ahmed, M. J., Chowdhury, M. T. I. (2004). A simple spectrophotometric method for the determination of cadmium in industrial, environmental, biological and soil samples using 5,7-dibromo-8-hydroxyquinoline. Anal. Sci., 20, 987–990. https://doi.org/10.2116/analsci.20.987