Egypt. J. Chem. **Vol. 67**, No. 11 pp. 111 - 124 (2024)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Ecofriendly Micelle Mediated Extraction (MME) and ICP OES Determination of Toxic Inorganic Pollutants from Environmental samples: Analytical characteristics and Mechanism study

Magda A. Akl[1*], Nora A. El-mahdy[1], H.E. Saad and El-Sayed R. H. El-Gharkawy[1]

[1] *Department of Chemistry, Faculty of Science, Mansoura University, Mansoura 35516, Egypt*

Abstract

In the present study, the N, O and S donor Isatin-3-(4-phenyl-3-thiosemicarbazone) (IPTS) formed hydrophobic complexes with Pd(II) and Co(II). Characterization of these complexes was carried out using various instrumental performances such as elemental analysis, Fourier transform infrared spectroscopy (FTIR), and UV-vis spectrophotometry. A micelle-mediated extraction (MME) method developed for the separation and enrichment of trace levels of palladium and cobalt was combined with inductively coupled plasma optical emission spectroscopy (ICP OES) to measure trace levels of palladium and cobalt in real samples. The hydrophobic Pd(II)-IPTS and Co(II)-IPTS complexes are extracted into the Triton X-114 rich phase. Parameters affecting both complexation and extraction, such as sample pH, IPTS and Triton X-114 concentrations, equilibration temperature, and time, are optimized. After the separation process, the Triton X-114 rich phase was diluted with acidic ethanol. Analyte concentrations were then determined by ICP OES. Under the optimal conditions chosen, the LOD, and LOQ for Pd(II) were 54 ngL-1, and 164 ngL-1, respectively. The LOD and the LOQ for Co(II) were 143ngL-1 and 432 ngL-1, respectively. This MME method was applied to real samples and recoveries of more than 95% were obtained in the spiked samples with a preconcentration factor of 100 and relative standard deviation less than 5% (n=5). The plausible mechanism of interaction between Triton X-114 and Pd(II)-IPTS and Co(II)-IPTS complexes is elucidated.

Keywords: IPTS, Cobalt (II) Palladium (II)TritonX-114 micelle-mediated extraction(MME)

1. Introduction

Separations and pre-concentration based on cloud point extractions are becoming a significant and practical application of the use of surfactants in analytical chemistry [1-3]. Using pre-concentration measures based on Micelle Mediated Extraction (MME) separation process provides a good option to more standard extraction processes [4-6] . The small quantity of the surfactant-rich step produced by this methodology enables easy, inexpensive, high-efficiency and reduced toxicity extraction methods to be used than extractions using organic solvents. MME also gives similar outcomes to those acquired with other methods of separation. Consequently, any species that interact with the micellar system, either directly (generally hydrophobic organic compounds) or after a preconditioned derivative reaction (e.g. metal ions after reaction with an appropriate hydrophobic ligand), may be extracted from the initial solution and may also be pre-concentrated. In hydrodynamic analytical processes such as liquid chromatography and capillary electrophoresis, the cloud point approach was used to separate and pre-concentrate organic compounds as a phase before they were determined [7-11].

In recent years, the use of micellar technologies such as MME has gained significant attention primarily because it is in accordance with the principles of "green chemistry". Green chemistry can be described as the methods used to reduce or eliminate the use or generation of toxic substances for human health and the environment[. For the following reasons, MME is a green method: (a) it uses diluted surfactant solutions as an extractor media that are inexpensive, resulting in the economy of reagents and the generation of few laboratory residues ; and (b)

*Corresponding author e-mail: magdaakl@yahoo.com.; (Prof Magda Akl).

EJCHEM use only: Received date 03 April 2023; revised date 04 April 2024; accepted date 02 May 2024

DOI: 10.21608/ejchem.2024.203822.7816

surfactants are not toxic, non-volatile and not easily flammable, unlike organic solvents used in liquid-liquid extraction.[12]

The use of the Micelle Mediated Extraction (MME) offers an interesting alternative to conventional extraction systems. Compared with conventional liquid-liquid solvent extraction, MMEP uses water and avoids the use of huge amounts of expensive, toxic, and flammable volatile organic solvents. Besides, MME can lead to higher extraction efficiency and a large concentration factor because the presence of the surfactant can minimize losses of analytes due to their adsorption into the container. [13] The MME technique has been used for extractive preconcentration, [14] separation, and/or purification of metallic species [15], metal chelates,[16] biomaterials,[17] and organic compounds.[18]

Extractions of metal ions by MME have been achieved in the absence of chelating extractants, [19], but Metal ion separation could be improved by the formation of sparingly water-soluble and hydrophobic complexes in the surfactant micellar solution using several chelating extractants Since Watanabe and Tanaka pioneered work [20] on nickel and zinc extraction, such as dithizone,[21],1-(2-thiazolylazo)-2-naphthol (TAN),[22], 1-(2-pyridylazo)-2- naphthol (PAN),[23]diethyldithiocarbamate (DDTC),[24], 8-hydroxyquinoline (HQ),[25] and *o*,*o*-diethyldithiophosphate (DDTP) [26]

Thiosemicarbazones constitute another family of powerful chelating extractants. Indeed, they are easy to be synthesized and have structural rigidity, and they are also used in selective solvent extraction of several kinds of metal cations. [27]

The polydentate Isatin-3-(4-phenyl-3-thiosemicarbazone) (IPTS), which acts as a good complexing agents through hydrazine nitrogen atom and thionate sulphur atom binding sites[28], was chosen as the chelating extractant because it forms more stable complexes than either O-O or N-N types. [29]

Cobalt is known to be important for metabolic processes at trace concentrations for humans, livestock and plants. It is clear that in the fields of environmental analysis, process control and medicine the determination of trace amounts of cobalt in biological and environmental samples is important(13-15). It is of excellent importance to determine trace quantities of cobalt in natural waters because cobalt is essential as complex vitamin B_{12} for living species. Cobalt deficiency in ruminants generally leads to various kinds of anemia. Toxicological impacts of big quantities of cobalt include human and animal vasodilatation, flushing and cardiomyopathy. Research on cobalt biochemistry in humans, microorganisms and enzymes has been extended [30-32].

The importance of palladium metal has evolved in latest years due to the growing applications for the manufacture of dental and medical instruments, jewelry and automotive catalytic converters [33-35]. Although the advantages of car catalysts are unquestionable, the environmental emission of palladium is mainly connected with the manufacture and recycling of catalytic converters in the metal finishing business as well as the operation of vehicle catalysts. Some of the compounds of palladium have been recorded as potential health hazards to humans causing asthma, allergy, rhino conjunctivitis, and other severe health issues. Therefore, developing analytical methods for palladium determination is essential for efficient control of this metal's pollution concentrations in the environment [36, 37].

The present study was carried out with the following objectives:

i. Design and the synthesis of the N, O and S donor Isatin-3-(4-phenyl-3-thiosemicarbazone) (IPTS) complexes with Pd(II) and Co(II).

ii. Characterization of Pd(II)-IPTS and Co(II)-IPTS complexes using various instrumental performances such as elemental analysis, Fourier transform infrared spectroscopy (FTIR), and UV-vis spectrophotometry.

iii. Pre-concentration, separation via Micelle Mediated Extraction and ICP OES determination of Pd(II) and Co(II) using IPTS ligand and TritonX-114

iv. To Study the optimum parameters affecting the MME like pH, concentration of metals, nonionic surfactant and ligand, incubation time and temperature.

v. Studying the applicability of the proposed MME-ICP OES methodology for the determination of Pd(II) and Co(II) in real water samples, synthetic mixtures and pharmaceutical samples.

vi. Elucidation of the plausible mechanisms involved in the process of interaction between Triton X-114 of Pd(II)-IPTS and Co(II)-IPTS complexes.

vii. Comparative evaluation of the present MME-ICP OES method with other previously reported methods.

2. Experimental

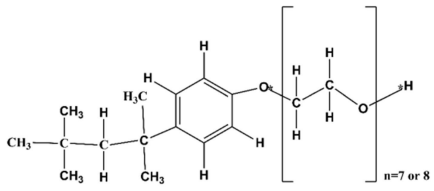
2.1. Instrumentation

Micelle Mediated Extraction (MME) pre-concentration experiments were done by using a thermostated bath maintained at the chosen temperature and phase separation was assisted using a centrifuge model of CH90-2 (Hinotek Technology Co. Ltd., China) was used to increase the phase separation process in 10 ml centrifuge tubes. Unicam

UV2100 UV/vis and MATTSON 5000 FTIR and inductivity coupled plasma–optical emission spectrometry (ICP OES) using a Varian spectrometer Model Varian Vista Pro, CCD Simultaneous, was used to register the spectral data and the measurements, respectively. The pH values of all solutions were measured with Hanna Instruments 8519 digital pH meter.

2.2. Reagents and solutions

All the chemicals which used in the current study are of analytical reagent grade. Double distilled water (DDW) was used. A stock solution of Cobalt (1000 mgL^{-1}) was prepared by dissolving 0.4037 g $CoCl_2.6H_2o$ in 100 ml of DDW with addition few drops of concentrated HCl. Palladium stock solution (100 mgL^{-1}) was prepared by dissolving 0.0216 g of $Pd(No_3)_2.2\ H_2o$ in 100 ml DDW by addition 1.0 ml of concentrated HNO_3. Triton X-114, Scheme 1, from Sigma Aldrich was prepared by dissolving 1 ml of triton X-114 in 5 ml ethyl alcohol. Then, complete to 100 ml DDW to obtain a stock solution of triton X-114 (1% v/v). Stock solution (1×10^{-3} $molL^{-1}$) of Isatin-3-(4-phenyl-3-thiosemicarbazone)(IPTS) was prepared by dissolving 0.0296 gm of IPTS in 100 ml ethyl alcohol.



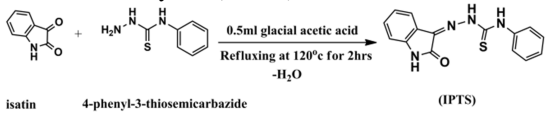
Scheme 1: Triton X-114

2.3. Preparations

2.3.1. Preparation of Isatin-3-(4-phenyl-3-thiosemicarbazone)

4-phenyl-3-thiosemicarbazide was prepared by mixing 6.7 ml from solution of phenyl isothiocyanate with 3 ml from solution of hydrazine hydrate, then added 10 ml ethyl alcohol. The final product was filtered and recrystallized from alcohol. M.p. 142℃ and yield (50.24%) [38].

Isatin-3-(4-phenyl-3-thiosemicarbazone) (IPTS) (Scheme 2) was synthesized as it was previously reported [38]. It is insoluble in methanol but easily soluble in acetone, ethanol, DMSO and DMF. m.p. was 240℃ and yield (63.5%)



Scheme2: Synthesis of Isatin-3-(4-phenyl-3-thiosemicarbazone) (IPTS)

2.3.2. Preparation of Co(II)- IPTS and Pd (II)-IPTS complexes

$CoCl_2.6H_2O$ (1 mmol, 0.2379 g) was dissolved in 10 ml of distilled water (DW) together with ligand (IPTS) (2 mmol, 0.5921 g) and refluxed for two hours at 100 ^oC to create the (Co-IPTS) complex. The system was then refluxed. The light orange tint of the solution changed to a violet precipitate during the process. Filtered precipitate cleaned repeatedly with water and ethanol before being vacuum dried.

Pd $(NO_3)_2.2H_2O$ (1 mmol, 0.2609 g) was dissolved in 10 ml of distilled water (DW) together with the ligand (IPTS) (1 mmol, 0.2961 g) and refluxed for two hours at 100 ^oC to create the palladium complex (Pd-IPTS). The system was then refluxed. The pale orange tint of the solution changed to a reddish-orange precipitate during the process. The precipitate has undergone filtering and many washings using water/ethanol, and then vacuum dried.

2.3.3. Sample analysis

Vials of vitamin B12 (hydroxocobalamin) were reviewed to confirm the cobalt content of each drug vial using the suggested method. Take 1 ml of each vial and heat in 5 ml of conc. HNO_3 for degradation. After cooling, the solution was filtrated and collected in a 50 ml volumetric flask. Then, complete with DDW at the mark.

2.4. MME Procedure

An aliquot of 10 ml of an aqueous solution containin g 2 g/L of Co II, 0.4 g/L of Pd II, either alone or in co mbination, and $2x10^4$ mol/L of IPTS, pH 4.5 (using 2 ml of acetate buffer), has been prepared for MME. F or 30 seconds, the mixture
was thoroughly agitated to ensure full complexation. 2ml of Triton X-
114 and 1 mL of NaCl solution (0.5 mol L-
1) were added to this combination.
The combination was then placed in a thermostatic ba th set at 70°C for 15 minutes. To separate the two pha ses, centrifuge at 3500 rpm for 10 minutes.
The mother aqueous phase was then easily separated after 10 minutes of
chilling the phases in an ice bath to improve their visc osity. To increase the sample volume and lower viscosity, the remaining micellar phase was dissolved in 3 ml of 1.0 $molL^{-1}$ HNO_3 in ethanol before being injected into the ICP OES for the simultaneous determination of Co (II) and Pd (II) in the organic phase at 236.379 and 340.458 nm, respectively.
The MME efficiency (S %) of Pd (II) and Co(II) was determined from the following relationship, Eq.1[4]:

$$S\% = (C_o/C_i) \times 100 \quad \text{(Eq.1)}$$

Here, C_o and C_i denote the concentration of each analyte in the micellar and in the initial aqueous layers, respectively.

Alternatively, Pd(II) and Co(II) were determined directly by ICP OES in the aqueous mother liquor. The separation efficiency (S %) of each analyte was calculated from its concentration in the mother liquor according to the relation, Eq.2 [4]:

$$S = [(c_i - c_f)/c_i] \times 100\ \%, \qquad \text{Eq.2}$$

where c_i and c_f denote the initial and final concentrations of the analyte, respectively.

Furthermore, 0.5 mL of methanol was added to the surfactant-rich phase and a 100 µL of the solution was transferred into a quartz cell containing the blank to measure the absorbance of the solution at 548 nm and 510nm for Pd(II) and Co(II), respectively.

The separation % (S, %) was calculated according to Eq.1 [4]

3. Results and discussion

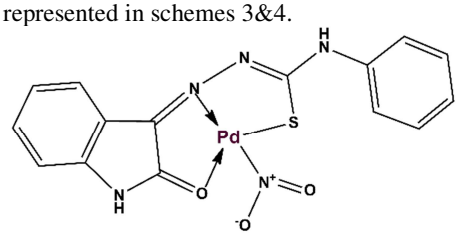
3.1. Method development

The optimized conditions of ICP-OES were presented in Table1. The synthesized IPTS and its metal complexes are stable at room temperature. The obtained metal complexes are colored and insoluble in water, ethanol and non-polar solvents. They have good solubility character in polar solvents i.e. DMF and DMSO.

Table 1: The optimized conditions for ICP OES for determination of Pd(II) and Co(II) ions

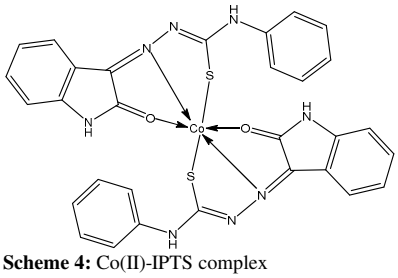
RF generator power (kW)	1.2	Pd wavelength (nm)	340.458
Frequency of RF generator (MHz)	40.68	Co wavelength (nm)	236.379
Plasma gas flow rate (l min^{-1})	12	Viewing height (mm)	9
Auxiliary gas flow rate (l min^{-1})	0.75	Pump rate (rpm)	15
Nebulizer pressure (kPa)	160		

The elemental analysis, FTIR and UV/visible spectra of the ligand and its metal complexes were performed. The structures of the metal complexes are represented in schemes 3&4.



$[Pd(IPTS)_2No_3]$

Scheme 3: Pd(II)-IPTS complex



Scheme 4: Co(II)-IPTS complex

3.2. Characterization

Pd(II) and Co(II) metal complexes derived from 1-isatin-4-phenyl-3-thiosemicarbazone (IPTS) have been synthesized and characterized on the basis of elemental analysis, and spectral (Visible, IR) measurements.

3.2.1. Elemental analysis

The elemental analysis of IPTS is presented in Table 2. The obtained results were in agreement with those calculated for the suggested formula. Anal. calc. (%): for IPTS; $C_{15}H_{12}N_4OS$; (296.07 g mol^{-1}); C, 60.8; H, 4.07; N, 18.90; found C, 60.2; H, 3.94; N, 18.62. Whereas, Anal. Calc. (%): for Co-IPTS & Pd-IPTS, respectively: C, 55.47; H, 3.41; N, 17.25 & C, 40.24; H, 2.48; N, 15.64; found C, 55.41; H, 3.39; N, 17.22 & C, 40.21; H, 2.45; N, 15.61.

3.2.2. FT-IR spectra

The most significant frequencies of both IPTS and its complexes in the FT-IR spectra are represented in Figure 5. IPTS exhibits an absorption band in the range from 3457 cm^{-1}, which can be assigned to the ν (OH) of the alcohol. The band at 3297 cm^{-1} is attributed to the ν(NH) vibrations of the ring of indole. The two bands at 1692 and 1594 cm^{-1} can be attributed to ν(C═O) of the isatin moiety and ν(C═N), correspondingly. The band detected at 1381 cm^{-1} is due to ν(C–N) groups. The bands at 1618, 782 and 3062 cm^{-1} are assigned to ν(C═C) groups, ν(C–H) and ν(═C–H) ring groups, respectively[39]. On the other hand, the FT-IR spectra of Co-IPTS and Pd-IPTS complexes indicate the bonding association of the ligand with the metal ion as found in Table 2. In contrast to the spectrum of the free ligand IPTS, in that of both complexes, we observed that there is a significant shift for the ν(OH), ν(NH), ν(C═N) and ν(C=O) vibrations. Meanwhile, the ν(C═C) vibration stays more or less in the same place, which indicates that (C═C) does not contribute to coordination with the metal ion. Also, there is a band appeared at1670, 1790 cm^{-1} in Co-IPTS and Pd-IPTS, respectively which indicates the presence of ν(C–S) group. Therefore, IR spectra show that IPTS coordinates in a tridentate manner via CN, CO and CS groups. This observation is

additionally supported by new bands that were found in the 595 and 623 cm^{-1} regions assigned to *ν*(Co–N) and *ν*(Pd–N), respectively[40].

Table 2. Analytical and some important physical measurements for IPTS

Assignments		IPTS	Co-IPTS	Pd-IPTS
Preparation Method		Reflux	Reflux	Reflux
Color		Light orange	Reddish-orange	Violet
Aspect		Powder	Powder	Powder
Melting Point (°C)		240	>300	>300
Reaction Time		2 hours	2 hrs	2 hrs
Yield (%)		63.5	88.1	86.2
Chemical Formula		$C_{15}H_{12}N_4OS$	$C_{30}H_{22}CoN_8O_2S_2$	$C_{15}H_{11}N_5O_3PdS$
Molecular Weight (g/mol)		296.07	649.06	447.76
Elemental analysis (Calc.) / Found	C %	(60.8)/ 60.2	55.47/55.41	40.24/40.21
	H %	(4.07)/ 3.94	3.41/3.39	2.48/2.45
	N %	(18.90)/ 18.62	17.25/17.22	15.64 /15.61
Characteristic infrared frequencies (cm^{-1})	ν(OH)	3457	2844	2875
	ν(NH)	3297	3000	3650
	ν(C=O)	1692	1875	1870
	ν(C=N)	1594	2280	2342
	ν(C-N)	1381	1275	1250
	ν(C-S)	1464	–	–
	ν(C=C)	–	1670	1970
	ν(C–H) fingerprint region	1618 782	1460 880-1000	1390 1092
	ν(=C–H) ring	3062		
	ν(Co–N)		595	
	ν(Pd–N)			623
UV- λ_{max} (nm)		366	480	572

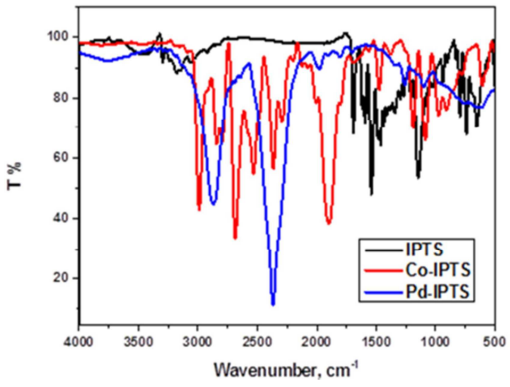


Figure 1: The FT-IR spectra of IPTS, and its complexes

3.2.3. UV-vis spectra

The electronic absorption spectra of the ligand and its metal complexes observed in DMF at room temperature are provided in Figures (2 and 3). From these figures, it can be established that IPTS reveals absorption band at 366 nm, which was assigned to intra ligand charge transfer (n–π* and π–π*). Meanwhile, both complexes reveals maximum absorption bands at 480 and 572 nm for Co-IPTS and Pd-IPTS, respectively which were assigned to ligand–metal charge transfer transitions (LMCT) and intra-ligand charge transfers (n–π* and π–π*) [41-45].

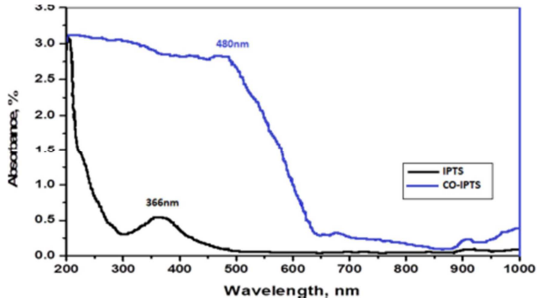


Figure 2: The electronic absorption spectra of IPTS, and Co-IPTS complex

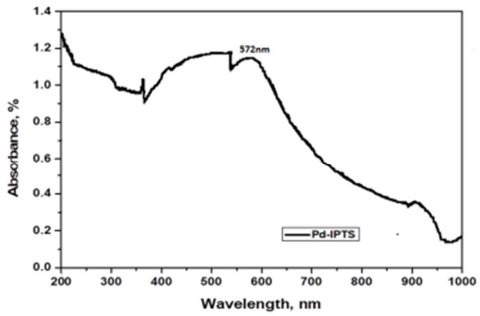


Figure 3: The electronic absorption spectra of Pd-IPTS complex

3.3. MME-ICP OES determination of Pd (II) and Co(II)

3.3.1. Effect of pH

The formation of metallic complex and its chemical stability are the two important factors involved in the separation and preconcentration of metal ions by Micelle Mediated Extraction(MME). They need to present sufficient hydrophobicity to be extracted into the small volume of the surfactant-rich phase. The pH of solution is the most important variable affecting metal ions removal. This is partly because hydrogen ions themselves are strongly competing with metal ions. Furthermore, the pH plays a critical role on metallic complex formation and subsequent extraction and has been a significant parameter for MME. [46]

For ionizable solutes, the charge of the solute can greatly influence its extent of binding to a micellar assembly. [47] The ionic form of a molecule normally does not interact with and bind the micellar aggregate as strongly as its neutral form. Indeed, adjustment of the micellar solution pH is the key parameter when controlling experimental variables in a Micelle Mediated Extraction process. [48]

In this study, the pH of sample solution was performed over wide rang 2 to 9 of buffer acetate. The experiments were carried out at the separation temperature of 65 °C. The extraction yield depends on the pH at which complex formation between metal ion and ligand occurs. It is evident that the Pd(II)-IPTS and Co(II)-IPTS H2L systems are reasonably influenced by the pH, as shown in Figure 4. The extraction yield reaches the highest amount at pH at pH 4-5 for Co (II) and Pd(II).

The pH of solution is the most important variable affecting metal ions removal. At lower pH values, the formation of complexes is not quantitative. The minimum extraction observed at low pH could be related to the higher concentration and mobility of H^+ ions, which is favored by high solubility and ionization of metallic salts in acid medium [49]. At higher pH values, the extraction starts to decrease.

The role of IPTS in the extraction (and hence determination) is demonstrated by comparing both curves with curve (a) that represents the analytes without IPTS (R%=30). A pH of 4.5 was selected to perform further extractions.

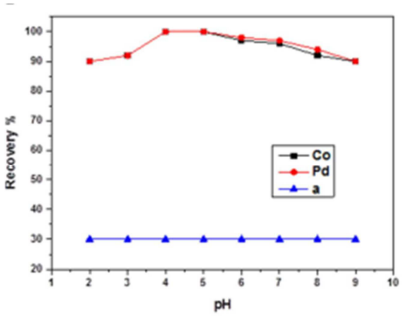


Figure 4: Effect of pH on CPE efficiency of 2x10-5 molL-1 Co(II) and Pd(II); (a) in the absence of IPTS; (Co, Pd) in the presence of 2x10-4 molL-1 IPTS by using 0.04 % (v/v) Triton X-114.

3.3.2. Effect of IPTS concentration

After the formation of sparingly water-soluble complexes, the MME is used for the preconcentration of metal ions. Its efficiency strongly depends on the hydrophobicity of the ligand and the complex formed in the miceller medium. Therefore, the effect of the amount of IPTS on the analytical responses was subsequently studied. The IPTS ligand is stable and hydrophobic chelating agent which reacts with both selected metal ions. Identical MME experiments were done by using 10^{-5} $molL^{-1}$ of IPTS chelating agent at pH 4.5 and 0.04 % (v/v) Triton X-114. The results obtained in Fig.5 Shows that the MME efficiency increases with increasing of ligand concentration until accomplished (≈100%) when M: IPTS is 1:2 and 1:1 for Co (II) and Pd(II), respectively. Excess amount of ligand has no opposite effect on the recovery, which facilities separation and determination of analytes unknown amounts. When the analyte concentration exceeds this ratio, the MME efficiency was declined. This decline occurs because of deficient amount of ligand for complete complexation and indirect separation. Consequently, a concentration of 2 $x10^{-4}$ $molL^{-1}$ IPTS was selected for the following work.

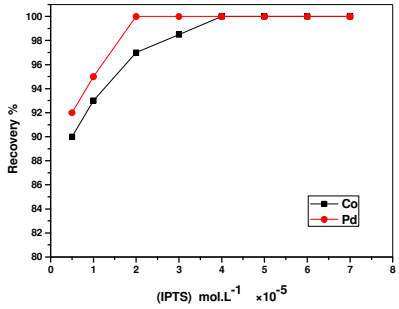


Figure 5: Effect of the IPTS concentration on the recovery of $2x10^{-5}$ $molL^{-1}$ Co(II) and Pd(II) in the presence of 0.04% (v/v) Triton X-114 at pH 4.5.

3.3.3. Effect of Triton X-114 concentration

Triton X-114 is a non-ionic surfactant and its available, commercial, low cost and toxicology so it was chosen. Additionally, it facilitates separation by using centrifuge and increase the density of the surfactant rich phase. Its concentration determines not only the result of extraction separation, but also the volume of the enriched micellar phase. The cloud point temperature of Triton X-114 allows its use in the pre-concentration of a large number of chelates and molecules (50-53). A $2×10^{-5}$ $molL^{-1}$ of (Co, Pd) was separated in the absence and presence of $2x10^{-4}$ $molL^{-1}$ of IPTS at pH 4.5 using different concentrations of Triton X-114. The results acquired in Fig. 6 present that the recovery % was 20% in the absence of IPTS and 100% in the presence of IPTS at 0.04 % (v/v) Triton X-114 for Co (II) and Pd (II). The decline in recovery % at high surfactant concentration may due be to the formation of a hydrated micelle coating on the solid surface. As a result, the hydrophobicity of the resulting surface was not acceptable for MME. 0.04 % (v/v) Triton X-114 for Co (II) and Pd (II) was selected for the extraction of analytes, but at low concentrations of surfactant, the recovery of complexes is poor because of a little amount of

surfactant molecules to entrap the hydrophobic chelating complexes quantitatively(54).

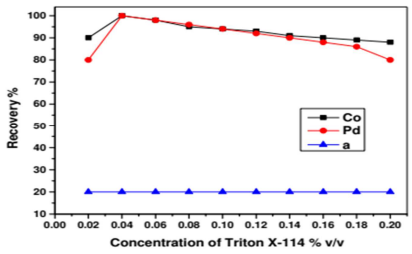


Figure 6: Influence of Triton X-114 concentration on the CPE efficiency of of 2×10^{-5} molL^{-1} of Co(II) and Pd(II) at pH 4.5 (a) in absence of IPTS, in the presence of $2x10^{-4}$ molL^{-1} IPTS at pH 4.5.

3.3.4. Effect of the incubation temperature and equilibration time

Two important factors in Micelle Mediated Extraction are equilibration temperature and incubation time. It is known that when MME is conducted using equilibration temperatures that are well above the cloud point temperature of the surfactant, the greatest analyte preconcentration factors will be obtained. It is desirable to employ the shortest incubation time and the lowest incubation temperature in order to ensure the completion of extraction and efficient separation of phases. Based on these reasons, the effect of equilibration temperature and time was examined. The dependence of extraction efficiency upon equilibration temperature and time above the cloud point in the range of 25–80°C and 5–30 min was thoroughly optimized, respectively (see Figures 7 and 8). [55]. The effect of temperature was performed under the previously optimum conditions of IPTS concentration, Triton X-114 concentration and pH. Over a wide range temperature (20-80℃) through incubation time 15 min. From Fig. 7, it was found the maximum separation occurred at range (60-80℃), so the adequate temperature is 70 ℃ for the both analytes. The effect of equilibration times was performed in the range 5-30 min. Fig. 8 explains that the quite incubation time achieved high recovery of Co (II) and Pd (II) ions is 15 min

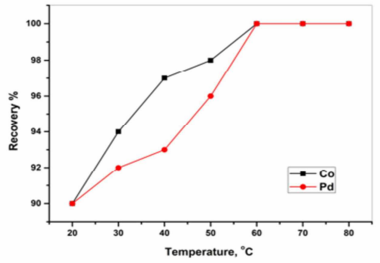


Figure 7: Effect of temperature on CPE recovery of Co(II) and Pd(II) in the presence of 2×10^{-4} molL^{-1} IPTS and 0.04 % (v/v) Triton X-114 at pH 4.5.

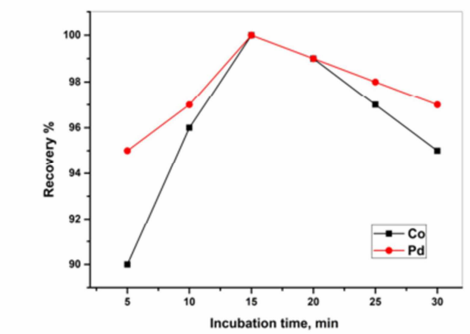


Figure 8: Effect of incubation time on CPE Recovery of Co(Ⅱ) and Pd(Ⅱ) in the presence of $2x10^{-4}$ molL^{-1} IPTS and 0.04 % (v/v) Triton X-114 at pH 4.5.

3.3.5. Effect of centrifugation time and rates

The effect of centrifuge rate was studied in the range 500-4000 rpm. The efficiency of the extraction increased with increasing the centrifugation rate from 500 to 4000 rpm and no difference was observed on the analytical signal above 4000 rpm. Thus, the centrifugation rate was chosen in our study is 3500 rpm. The effect of centrifuge time was studied in range 5-30 min. From Fig. 9, the centrifugation time was selected in the range (10-15 min) and had a significant effect on the analytical signal is 10 min at 3500 rpm for both metal ions.

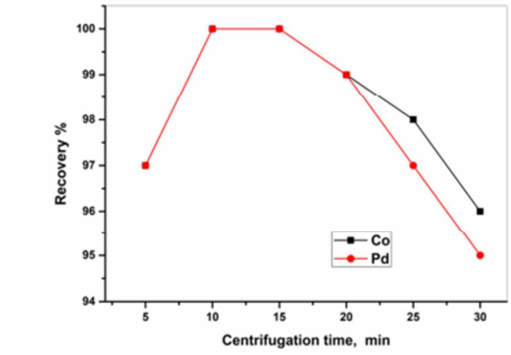


Figure 9: Effect of centrifugation time on CPE Recovery of Co(Ⅱ) and Pd(Ⅱ) in the presence of $2x10^{-4}$ molL^{-1} IPTS and 0.04 % (v/v) Triton X-114 at pH 4.5.

3.3.6. Effect of electrolyte (KCl)

MME can be controlled by adding salts or some organic complexes (salting-out effect). The effect of KCl concentration was studied in the range of 0.01-0.1 M. It was noted that the efficiency of the extraction of both cations increased with increase the KCl concentration. The KCl concentration of 0.04 M was chosen the best concentration had a significant

effect on the extraction efficiency for Co (Ⅱ) and Pd(Ⅱ) ions.

3.3.7. Influence of sample volume

A series of experiments were conducted to extract a fixed concentration of each analyte ($2.0x10^{-5}$ mol L^{-1}) from different aqueous volumes (50–1500 ml) under the recommended conditions. The results obtained revealed that $2x10^{-5}$ $molL^{-1}$ of each analyte can be quantitatively separated from different aqueous volumes up to 1 liter using 10 mL of the organic layer. The enrichment factor (preconcentration factor), defined as the ratio of the volumes before and after MME, was 100.

3.3.8. Effect of interfering ions

The effect of interfering ions was studied by using $2x10^{-5}$ $molL^{-1}$ for Co (II) and Pd (II), (n=3) in the presence of excess amount of IPTS $2x10^{-4}$ $molL^{-1}$ of IPTS at pH 4.5 and room temperature. The presented in Table 3 explain the various effects of the interfering ions on both analytes.

Table 3: Tolerance limits for the determination of $2x10^{-5}$ $molL^{-1}$ for Co (II) and Pd (II), (n=3) in the presence of $2x10^{-4}$ $molL^{-1}$ of IPTS at pH 4.5 and room temperature.

Foreign ions	Concentration (µg mL^{-1})	Recovery %	
		Co(Ⅱ)	Pd(Ⅱ)
Cd^{+2}	20	98.7	98.5
Ni^{+2}	20	98.8	98.2
Zn^{+2}	20	98.8	98.4
Mn^{+2}	20	99	99.2
Hg^{+2}	10	98.7	98.8
Ba^{+2}	20	99.1	99
Cr^{+3}	10	98.7	99.5
Cu^{+2}	20	99	98.9
Fe^{+3}	20	98.8	98.5
Bi^{+3}	20	98.7	98
Al^{+3}	20	98.9	99
Cl^{-}	177.5	98.5	97.2
SO_4^{--}	300	97.5	100
NO_3^{-}	310	98.2	100
CH_3COO^{-}	295	99	98
NO_2^{-}	230	97.8	98.7

3.3.9 Analytical characteristics

Under the previous experimental conditions, calibration graphs were achieved by pre-concentration of the sample 10 ml which containing a known amounts of the both analytes. Under specified recommended conditions the calibration graphs of Co(II) and Pd(Ⅱ) had a good linearity in the range of (0.5-5.0 µg mL^{-1}) and (0.1-1.5 µg mL^{-1}) respectively, with a limit of detection (LOD) is established on three times the standard deviation of the blank divided by the slope of the analytical graph (*3S/b*), was 0. 143 µg L^{-1} for Co(II) and 0.054 µgL^{-1} for Pd(II). (n=3). The analytical parameters of the proposed method (MME) are illustrated in Table 4. The relative standard deviation(RSD,%), as a measure of the precision of the present MME procedure was determined to be less than 2.0 % for Co(Ⅱ) and Pd(Ⅱ)

Table 4: Analytical characteristics of the calibration graphs of the analytes

Analyte	Co(II)	Pd(II)
Linear range, µg mL^{-1}	0.5-5	0.3-1.5
Regression equation*	A=0.34667C+ 0.0467	A=0.63981C+ 0.02754
Correlation coefficient	0.9915	0.9997
LOD, µgL^{-1}	0.143	0.054
LOQ, µgL^{-1}	0.432	0.164
RSD %	1.48	1.19
Sample volume, ml	10	10

*A=Absorbance, C=concentration, relative standard deviation (RSD), Limit of detection (LOD)

3.3. 10. Applications

3.3.10.1. Analysis of water samples

In order to investigate the applicability to natural-water samples, the recoveries of known amounts of Pd(II) and Co(II) added to distilled water, Nile water, Tap water and sea water samples were examined by such a procedure. To 20 ml aliquots of clear uncontaminated, filtered water samples 1, 3 and 5 µg of Pd(II) or Co(II) were added and the pH was adjusted to pH 4.5. After MME (as previously mentioned), 0.5 mL of methanol was added to the surfactant-rich phase and a 100 µL of the solution was transferred into a quartz cell containing the blank to measure the absorbance of the solution at 548 nm and xxx for Pd(II) and Co(II), respectively. The separation % (S, %) was calculated according to Eq.1. The results are given in Table 5. It is worth noting that, a parallel series of the same experiments were carried out under the same conditions, and that the palladium content was completely eluted and introduced directly into for a Pd(II) ICPOES as a confirmatory test. The results revealed that high confirmation is gained. The data given in Table 3 demonstrates that the technique is applicable to the analysis of Pd(II) and Co(II) in different water samples, and is satisfactory.

3.3.10.2. Analysis of pharmaceutical samples

Under the achieved conditions, MME was applied then followed by FAAS to determine Co (Ⅱ) in some pharmaceutical samples (Vitamin B12 ampules). The perfect results were acquired and the reported data was in Table 6.

3.3.10.3. Synthetic mixtures Application

Numerous synthetic mixtures of 10 ml of aqueous sample solution which containing different

compositions of various metal ions and the analytes of known concentrations, $2x10^{-4}$ $molL^{-1}$ of IPTS and 0.04% (v/v) of Triton X-114 at pH 4.5 for Co(Ⅱ) and Pd(Ⅱ). The procedures of MME were done under previous optimized conditions and the recoveries of the analytes were determined in the presence of various concentrations of interfered ions by using ICP OES. The results obtained in Table 7 shows that good recoveries of the analytes were achieved in all mixtures.

Table 5: Recovery of Co (II) and Pd(II) in different water samples (n=3) after CPE using $2x10^{-4}$ $molL^{-1}$ of IPTS at pH 4.5 and room temperature.

Types of water (location)	Co (Ⅱ), µg mL^{-1}		Pd (Ⅱ), µg mL^{-1}		Recovery, %		RSD, %	
	added	Found	Added	Found	Co(Ⅱ)	Pd(Ⅱ)	Co(Ⅱ)	Pd(Ⅱ)
Distilled water	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	3.00	2.97	1.00	0.98	99	98	1.00	0.70
	6.00	5.898	3.00	2.919	98.3	97.3	0.70	0.70
	9.00	8.892	5.00	4.91	98.8	98.2	0.78	0.71
Tap water (our laboratory)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	3.00	2.91	1.00	0.996	97	99.6	1.41	0.15
	6.00	5.796	3.00	2.994	96.6	99.8	1.58	0.16
	9.00	8.793	5.00	4.97	97.7	99.4	2.23	2.5
Nile water (Mansoura city)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	3.00	2.96	1.00	0.982	98.6	98.2	0.15	1.58
	6.00	5.898	3.00	2.99	98.3	99.6	1.58	1.57
	9.00	8.802	5.00	4.96	97.8	99.2	2.23	2.64
Sea water (Marsa Matrouh)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	3.00	2.961	1.00	0.988	98.7	98.8	0.55	0.70
	6.00	5.91	3.00	2.92	98.5	97.3	0.75	1
	9.00	8.793	5.00	4.96	97.7	99.2	1.63	1

Relative standard deviation (RSD)

Table 6: Statistical evaluation for analysis of some pharmaceutical vitamin samples after CPE (n=3). Comparison of experimental mean ($\bar{X}$) mg/ampule with true value (µ), by $|t|_1$ test.

Sample	($\bar{X}$)	µ	S	$\|t\|_1$	RSD, %
No. 1 Biovit 12 (Medical Union Pharm) ampule	1.99	2.00	0.01	1.73	1.5
No. 2 Depovit B12(Amriya Pharm) ampule	1.98	2.00	0.02	1.73	2.3

($\bar{X}$): experimental value, (µ) true value; $|t|_1$ for P = 0.05 and n=3 (2 degree of freedom) = 4.303. R.S.D., %: Relative standard deviation.

Statistical parameters: n = 5, $\pm ts/\sqrt{n}$, s = standard deviation, t = student factor, p = 0.05.

Table 7: Recovery of Co (II) and Pd (II) from synthetic mixtures (n=3) in the presence of $2x10^{-4}$ $molL^{-1}$ of IPTS at pH 4.5 and room temperature

Synthetic mixtures composition (µg mL^{-1})	Concentration added of each of Co(II) and Pd(II)(µg mL^{-1})	Co(Ⅱ) (µg ml^{-1})		Pd(Ⅱ) (µg ml^{-1})	
		founded	R %	founded	R %
$Pb^{+2} + Hg^{+2}$	2.00	1.96	98	1.95	97.5
$Mn^{+2} + Ni^{+2}$	2	1.98	99	1.97	98.5
$Pb^{+2} + Hg^{+2} + Ba^{+2}$	3	2.97	99	2.98	99.3
$Fe^{+3} + Cr^{+3} + Al^{+3}$	3	2.98	99.3	2.96	98.7
$Ni^{+2} + Ba^{+2} + Cr^{+3} + Al^{+3}$	4	3.89	97.2	3.91	97.7
$Ag^{+} + Au^{+2} + Ni^{+2} + Zn^{+2}$	4	3.90	97.5	3.88	97

3.3.11. The plausible Mechanism of the interaction between Triton X-114 surfactant and Pd(II)-IPTS and Co(II)-IPTS complexes

Initially, in MME extraction, a micellar (surfactant-rich) phase is added to the sample which is originated from homogeneous surfactant solution. A non-polar core is developed due to its hydrocarbon tails towards the center by a micelle [58]. The, the separation of compounds occurs in the hydrophobic core of micelles. During heating, cloud is generated due to nonionic surfactants. These clouds then form two coexisting isotropic phases. At a specific temperature, also called as clouding point temperature, surfactant-rich and a surfactant-lean phases are formed due to physical change in the homogeneous solutions of amphiphilic substances. Because of the attraction a cluster is formed. The mechanism by which this separation occurs is attributed due to the rapid increase in aggregation number of the surfactant's micelles, as a result of the increase in temperature, or any other critical phenomena (Fig. 10). This effect causes a decrease in the effective area occupied by the polar group on the micelle surface, increasing the size of the micelle that can be considered to become infinite at the cloud point, resulting in phase separation.

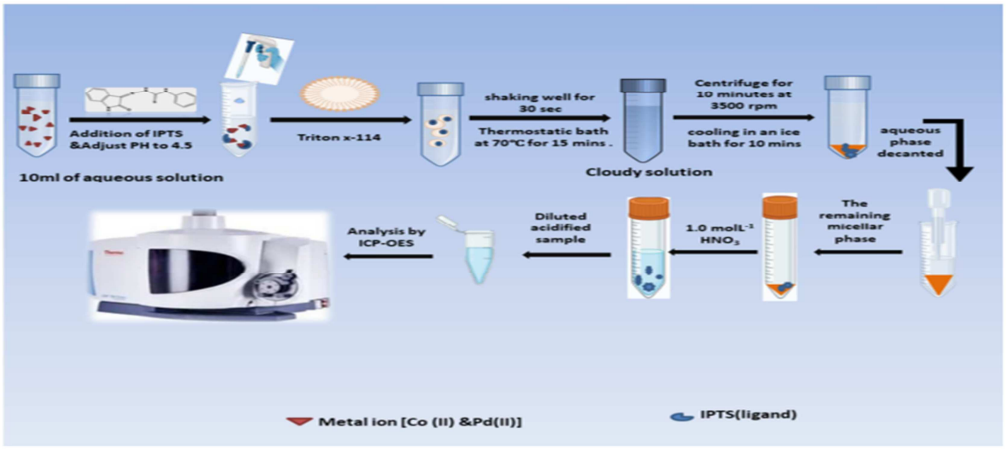
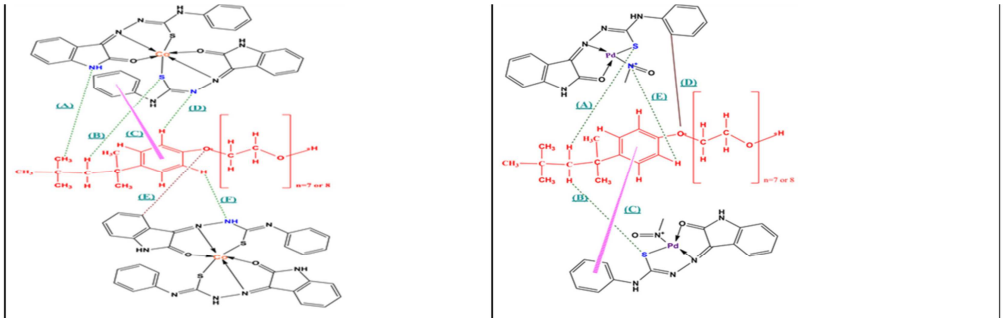


Figure 10 CPE of Pd(II) and Co(II) using IPTS extractant and Triton X-114 nonionic surfactant

The plausible interaction between Triton X-114 surfactant and Pd(II)-ISPT and Co(II)-ISPT complexes is schematically represented in Figure 11. Triton X-114 surfactant is immiscible with water molecules, which is more favorable for effective separation of Pd(II)-ISPT and Co(II)-ISPT complexes from water. There are also several chemical and physical interactions occurring between Triton X-114 surfactant and Pd(II)-ISPT and Co(II)-ISPT complexes such as orbital interaction, charge-charge interaction, and hydrogen bond interaction with neutral molecules, van der Waals interaction between alkyl chain, CH-π interaction, π-π interaction, and n-π interaction (Figure 11) [57–60].



(i) The possible molecular interaction at molecular level between Triton X-114 and Co(II)-ISPT	(ii) The possible molecular interaction at molecular level between Triton X-114 and Pd(II)-ISPT
(A) H (surfactant triton x-114) – N (Co- complex) interaction. (B) H (surfactant triton x-114) - S (Co-complex) interaction. (C) π (surfactant triton x-114) - π (Co-complex) interaction. (D)H (surfactant triton x-114) - N (Co-complex) interaction. (E) O (surfactant triton x-114) – H (Co- complex) interaction. (F) H (surfactant triton x-114) – N (Co- complex) interaction.	(A) H (surfactant triton x-114) – S (Pd- complex) interaction. (B) H (surfactant triton x-114) - S (Pd-complex) interaction. (C) π (surfactant triton x-114) - π (Pd-complex) interaction. (D) O (surfactant triton x-114) - H (Pd-complex) interaction. (E) H (surfactant triton x-114) – N (Pd- complex) interaction

Figure 11 The plausible interaction at molecular level between Triton X-114 and (i) Co(II)-ISPT; (ii) Pd(II)-ISPT complexes

3.3.12. Performance of the proposed IPTS

In order to enhance the value of method, we carried out a comparative study of the detection limit of cobalt and palladium obtained from the present study obtained for the same pollutant to other methods reported in the literature. Table 8 grouped together the different values of detection limit of cobalt and palladium for the different methods. We can see that the detection limit of cobalt and palladium observed in the present study is well positioned with respect to other researches with a LOD(µg L^{-1}) of 0.1430 and 0.054 for Co(II) and Pd(II), respectively, relatively, interesting compared to other methods. The differences of the LOD of Co(II) and Pd(II) ions are due to the properties of each ligand like the structure, the functional groups and the method of determination. IPTS could be an attractive ligand owing to its N and S donor sites. In the future, the biological activities of different IPTS derived complexes will be investigated. Moreover, modification dialdehyde cellulose from agro-residues using IPTS, can be implemented to be applied in the wastewater treatment plant for cationic and anionic textile dye removal from wastewater.

Table 8: Comparative table for determination of cobalt and palladium in different types of samples applying CPE before analysis by ICP OES

Reagent	Surfactant	Sample volume(mL)	Element	LOD (µg mL^{-1})	Sample	Detection	Reference
APDC	Triton X-114	10	Co	2.1	Biological tissues	TS-FF-FAAS	[61]
APDC	Triton X-114	10	Co	5.0	Water	FAAS	[62]
ACDA	Triton X-114	10	Co	7.5	Water	SP	[63]
Me- BTABr	Triton X-114	10	Co	0.9	Water	FAAS	[64]
IPTS	Triton X-114	10	Co	0.143	Water	ICP-OES	This work
PMBP	PONPE 7.5	10	Pd	0.0018	Mine samples	FAAS	[65]
DDTP	Triton X-114	10	Pd	1.4×10^{-5}	Blood	ETAAS	[66]
PAN	Triton X-114	10	Pd	4×10^{-5}	Water	TLS	[67]
IPTS	Triton X-114	10	Pd	0.054	Water	ICP-OES	This work

Reagent	Surfactant	Sample volume(mL)	Element	LOD (µg mL^{-1})	Sample	Detection	Reference
APDC	Triton X-114	10	Co	2.1	Biological tissues	TS-FF-FAAS	[61]
APDC	Triton X-114	10	Co	5.0	Water	FAAS	[62]
ACDA	Triton X-114	10	Co	7.5	Water	SP	[63]
Me- BTABr	Triton X-114	10	Co	0.9	Water	FAAS	[64]
IPTS	Triton X-114	10	Co	0.143	Water	ICP-OES	This work
PMBP	PONPE 7.5	10	Pd	0.0018	Mine samples	FAAS	[65]
DDTP	Triton X-114	10	Pd	1.4×10^{-5}	Blood	ETAAS	[66]
PAN	Triton X-114	10	Pd	4×10^{-5}	Water	TLS	[67]
IPTS	Triton X-114	10	Pd	0.054	Water	ICP-OES	This work

4. Conclusion

In this study, the combined advantages of the Micelle Mediated Extraction process and the use of a polydentate Isatin-3-(4-phenyl-3-thiosemicarbazone) (IPTS) as extractant were utilized for extraction of palladium(II) and cobalt(II) in different real samples. From the results obtained, the following conclusions can be drawn:

(i) The complexes of Pd(II) and Co(II) with IPTS were simply synthesized and characterized by elemental analysis, FTIR and UV-vis spectroscopic performances.

(ii) The IPTS acts as a polydentate extractant that chelates with Pd(II) and Co(II) through the N and S donor sites.

(iii) The Isatin-3-(4-phenyl-3-thiosemicarbazone) (IPTS) proved to be an efficient chelating extractant for quantitative Micelle Mediated Extraction of palladium(II) and cobalt(II). The simple synthesis, the formation of stable complexes, and consistency with the Micelle Mediated Extraction process are the major advantages of the use of this type of extractants in Micelle Mediated Extraction of Pd(II) and Co(II).

(iv) The extent of extraction is markedly influenced by the pH of the aqueous solution and the concentration of the extractant and nonionic surfactant.

(v) The good biodegradability of the nonionic surfactant and the easy disposal of the small volume fraction of the aqueous surfactant rich phase are

particularly attractive for processes adopting green chemistry practices.

(vi) The nature of the interaction and binding between the extracted species with this kind of extractant and the nonionic surfactant micelles.

5. References

1. Mandal S, Lahiri S. A review on extraction, preconcentration and speciation of metal ions by sustainable cloud point extraction. Microchemical Journal. 2022;175:107150.
2. Milcheva NP, Genc F, Racheva PV, Delchev VB, Andruch V, Gavazov KB. An environmentally friendly cloud point extraction–spectrophotometric determination of trace vanadium using a novel reagent. Journal of Molecular Liquids. 2021;334:116086.
3. Racheva PV, Milcheva NP, Genc F, Gavazov KB. A centrifuge-less cloud point extraction-spectrophotometric determination of copper (II) using 6-hexyl-4-(2-thiazolylazo) resorcinol. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2021;262:120106.
4. Akl M, Bekheit M, Helmy I. Application of CPE-FAAS methodology for the analysis of trace heavy metals in real samples using phenanthraquinone monophenyl thiosemicarbazone and triton X-114. J Anal Bioanal Tech. 2016;7(325):2.
5. Akl ZF. Sensitive quantification of uranium using cloud point extraction coupled with inductively coupled plasma-optical emission spectrometry. Journal of Radioanalytical and Nuclear Chemistry. 2018;315(1):21-8.
6. Akl MA, AL-Rabasi A, Molouk AF. Cloud point extraction and FAAS determination of copper (II) at trace level in environmental samples using N-benzamido-N'-benzoylthiocarbamide and CTAB. Egyptian Journal of Chemistry. 2021;64(1):313-22.
7. Hasheminasab KS, Fakhari AR. Application of nonionic surfactant as a new method for the enhancement of electromembrane extraction performance for determination of basic drugs in biological samples. Journal of Chromatography A. 2015;1378:1-7.
8. Takla SS, Shawky E, Hammoda HM, Darwish FA. Green techniques in comparison to conventional ones in the extraction of Amaryllidaceae alkaloids: Best solvents selection and parameters optimization. Journal of Chromatography A. 2018;1567:99-110.
9. Saridal K, Ulusoy Hİ. A simple methodology based on cloud point extraction prior to HPLC-PDA analysis for tetracycline residues in food samples. Microchemical Journal. 2019;150:104170.
10. Flores K, Turley RS, Valdes C, Ye Y, Cantu J, Hernandez-Viezcas JA, et al. Environmental applications and recent innovations in single particle inductively coupled plasma mass spectrometry (SP-ICP-MS). Applied Spectroscopy Reviews. 2021;56(1):1-26.
11. Mortada WI, Alharthi S. Preconcentration of aluminum by dual-cloud point extraction and its determination by inductively coupled plasma-optical emission spectrometry. Current Analytical Chemistry. 2021;17(9):1365-72.
12. Mortada WI. Recent developments and applications of cloud point extraction: A critical review. Microchemical Journal. 2020;157:105055.
13. Sicilia, D.; Rubio, S.; Pe´rez-Bendito, D.; Maniasso, N; Zagatto, E. A. G. Anionic surfactants in acid media: a new cloud point extraction approach for the determination of polycyclic aromatic hydrocarbons in environmental samples. *Anal. Chim. Acta* **1999**, *392*, 29–38.
14. Hinze, W. L.; Pramauro, E. A critical-review of surfactant-mediated phase separation (cloud point extraction)-theory and applications. *Crit. Re*V. *Anal. Chem.* **1993**, *24*, 133–177.
15. Stalikas, C. D. Micelle-mediated extraction as a tool for separation and preconcentration in metal analysis. *Trends Anal. Chem.* **2002**, *21*, 343–355.
16. Tani, H.; Kamidate, T.; Watanabe, H. Micelle-mediated extraction. *J. Chromatogr. A* **1997**, *780*, 229–241.
17. Tani, H.; Kamidate, T.; Watanabe, H. Aqueous micellar two-phase systems for protein separation. *Anal. Sci.* **1998**, *14*, 875–888.
18. Li, J.; Chen, B.-H. Equilibrium partition of polycyclic aromatic hydrocarbons in a cloud-point extraction process. *J. Colloid Interface Sci.* **2003**, *263*, 625–632.
19. Akita, S.; Rovira, M.; Sastre, A. M.; Takeuchi, H. Cloud Point extraction of gold (III) with non-ionic surfactant. Fundamental and its application to gold recovery from printed substrate. *Sep. Sci. Technol.* **1998**, *33*, 2159–2177.
20. Watanabe, H.; Tanaka, H. A non-ionic surfactant as a new solvent for liquid extraction of Zinc (II) with 1-(2-pyridylazol)-2-naphlhol. *Talanta* **1978**, *25*, 585–589.
21. Garrido, M.; Di-Nezio, M. S.; Lista, A. G.; Palomeque, M.; Fernadez-Band, B. S. Cloud-Point extraction/preconcentration On-Line FiaMethod For Mercury Determination. *Anal. Chim. Acta* **2004**, *502*, 173–177.
22. Teo, K. C.; Chen, J. Determination of manganese in water samples by flame atomic absorption spectrometry after cloud point extraction. *Analyst* **2001**, *126*, 534–537.
23. Doroschuck, V. O.; Lelyushok, S. O.; Ishchenko, V. B.; Kulichenko, S. A. Flame atomic absorption determination of manganese (II) in natural water after cloud point extraction. *Talanta* **2004**, *64*, 853–856.
24. Yuan, C. G.; Jiang, G. B.; Cai, Y. O.; He, B.; Liu, J. F. Determination of cadmium at the nanogram per liter level in seawater by graphite furnace AAS using cloud point extraction. *At. Spectrosc.* **2004**, *25*, 170–176.
25. Shimerani, F.; Abkenar, S. D.; Jamali, M. R. Determination of cadmium(II), copper(II) and

zinc (II) in water samples by flame atomic absorption spectrometry after cloud point extraction. *Indian J. Chem., Sect. A* **2005**, *44*, 1211–1214.
26. Manzoori, J. L.; Bavili, A. T. Cloud point preconcentration and flame atomic absorption spectrometric determination of Cd and Pb in human hair. *Anal. Chim. Acta* **2002**, *470*, 215–221.
27. Spinu, C.; Kriza, A. Co(II), Ni(II) and Cu(II) Complexes of bidentate Schiff bases. *Acta Chim. Slo*V. **2000**, *47*, 179–185.
28. Gupta S, Singh N, Khan T, Joshi S. Thiosemicarbazone derivatives of transition metals as multi-target drugs: A Review. Results in Chemistry. 2022:100459.
(29) Sone, K.; Fukuda, Y. *Inorganic Thermochromism (Inorganic Chemistry Concept)*; Springer: Heidelberg, 1987; Vol. 10.
30. Barceloux DG, Barceloux D. Cobalt. Journal of Toxicology: Clinical Toxicology. 1999;37(2):201-16.
31 Czarnek K, Terpiłowska S, Siwicki AK. Selected aspects of the action of cobalt ions in the human body. Central European Journal of Immunology. 2015;40(2):236-42.
32. González-Montaña J-R, Escalera-Valente F, Alonso AJ, Lomillos JM, Robles R, Alonso ME. Relationship between vitamin B12 and cobalt metabolism in domestic ruminant: an update. Animals. 2020;10(10):1855.
33. Mohammadi SZ, Mohammadnezhad M. Selective ligandless cloud point extraction of palladium from water and dust samples. Journal of AOAC International. 2015;98(1):201-5.
34. Rinkovec J. Platinum, palladium, and rhodium in airborne particulate matter. Arhiv za higijenu rada i toksikologiju. 2019;70(4):224-30.
35. Hughes AE, Haque N, Northey SA, Giddey S. Platinum group metals: A review of resources, production and usage with a focus on catalysts. Resources. 2021;10(9):93.
36. Cutler CP. Use of metals in our society. Metal allergy: Springer; 2018. p. 3-16.
37. Samim M. Palladium nanoparticles as emerging pollutants from motor vehicles: An in-depth review on distribution, uptake and toxicological effects in occupational and living environment. Science of The Total Environment. 2022:153787.
38. Gupta R, Yadav B, Srivastava AK, editors. Synthesis of some Mannich bases of isatin-3-(4′-phenyl-3′-thiosemicarbazone) and their antibacterial activity. Proceedings of the Indian Academy of Sciences-Chemical Sciences; 1985: Springer.
39. Enamullah M, Zaman MA-m, Bindu MM, Islam MK, Islam MA. Experimental and theoretical studies on isatin-Schiff bases and their copper (II)-complexes: Syntheses, spectroscopy, tautomerism, redox potentials, EPR, PXRD and DFT/TDDFT. Journal of Molecular Structure. 2020;1201:127207.
40. Ramesh G, Daravath S, Ganji N, Rambabu A, Venkateswarlu K. Facile synthesis, structural characterization, DNA binding, incision evaluation, antioxidant and antimicrobial activity studies of Cobalt (II), Nickle (II) and Copper (II) complexes of 3-amino-5-(4-fluorophenyl) isoxazole derivatives. Journal of Molecular Structure. 2020;1202:127338.
41. Lakshmi Praveen P, Ojha DP. Photosensitivity, substituent and solvent-induced shifts in UV-visible absorption bands of naphthyl-ester liquid crystals: a comparative theoretical approach. Liquid Crystals. 2014;41(6):872-82.
42. Das P, Praveen PL, editors. Theoretical investigation on absorption spectral profile of tetrazole liquid crystals: Hexyl, nonyl end groups and solvent effects. IOP Conference Series: Materials Science and Engineering; 2020: IOP Publishing.
43. Praveen PL. Nematic and smectic bithiophenes for UV sensing mechanism: Comparative calculations on different homologues. Journal of Molecular Liquids. 2021;341:117424.
44. Praveen PL, DS R, Ojha DP. UV spectral characterization of a smectic-C liquid crystal: theoretical support to the experiment. Molecular Crystals and Liquid Crystals. 2017;643(1):76-82.
45 Akl Magda A., Nora A. El-Mahdy & El-Sayed R. H. El-Gharkawy Design, structural, spectral, DFT and analytical studies of novel nano-palladium Schiff base complex Scientific Reports | (2022c) 12:17451 |
46. Shangzhi Wang, Shuangming Meng, and Yong Guo Cloud Point Extraction for the Determination of Trace Amounts of Cobalt in Water and Food Samples by Flame Atomic Absorption Spectrometry Journal of Spectroscopy 2013, Article ID 735702, 7 pages
47. Fendler, J. H. Atomic and molecular clusters in membrane mimetic chemistry. *Chem. Re*V. **1987**, *87*, 877–899.
48. H Reffas, T Benabdallah, M H Youcef, and H Ilikti Study on the Cloud Point Extraction of Copper(II) from an Aqueous Sulfate Medium with *N*,*N*′-Bis(salicylideneaminoethyl)amine Polydentate Schiff Base into a Nonionic Surfactant Phase *J. Chem. Eng. Data* 2010, *55,* 912–918
49. Y.B. Onundi, A.A. Mamun, M.F. Al Khatib, M.A. Al Saadi, A.M. Suleyman, Heavy metals removal from synthetic wastewater by a novel nano-size composite adsorbent, Int. J. Environ. Sci. Technol. 8 (4) (2011) 799–806.
50. Silva MF, Fernandez L, Olsina RA, Stacchiola D. Cloud point extraction, preconcentration and spectrophotometric determination of erbium (III)-2-(3, 5-dichloro-2-pyridylazo)-5-dimethylaminophenol. Analytica chimica acta. 1997;342(2-3):229-38.
51. Chen J, Teo KC. Determination of cobalt and nickel in water samples by flame atomic absorption spectrometry after cloud point extraction. Analytica Chimica Acta. 2001;434(2):325-30.
52. Sombra L, Luconi M, Silva MF, Olsina RA, Fernandez L. Spectrophotometric determination of trace aluminium content in parenteral solutions by combined cloud point preconcentration–flow injection analysis. Analyst. 2001;126(7):1172-6.

53. Silva MF, Olsina RA. Monitoring the elimination of gadolinium-based pharmaceuticals. Cloud point preconcentration and spectrophotometric determination of Gd (III)-2-(3, 5-dichloro-2-pyridylazo)-5-dimethylaminophenol in urine. Analyst. 1998;123(9):1803-7.
54. Khalifa ME, Akl MA, Ghazy SE-S. Selective flotation-spectrophotometric determination of trace copper (II) in natural waters, human blood and drug samples using phenanthraquinone monophenylthiosemicarbazone. Chemical and pharmaceutical bulletin. 2001;49(6):664-8.
55. Frankewich RP, Hinze WL. Evaluation and optimization of the factors affecting nonionic surfactant-mediated phase separations. Analytical Chemistry. 1994;66(7):944-54.
56. Melnyk A, Namies´nik J, Wolska L (2015) Theory and recentapplications of coacervate-based extraction techniques. TrAC Trends Anal Chem 71:282–292. https://doi.org/10.1016/j.trac.2015.03.013
57. A. M. Fernandes, M. A. A. Rocha, M. G. Freire, I.M.Marrucho, J. A. P. Coutinho, and L. M. N. B. F. Santos, "Evaluation of cation-anion interaction strength in ionic liquids," *The Journal of Physical Chemistry B*, vol. 115, no. 14, pp. 4033–4041, 2011.
58. R. L¨u, J. Lin, and Z. Qu, "Theoretical study on interactions between thiophene/dibenzothiophene/cyclohexane/toluene and 1-methyl-3-octylimidazolium tetrafluoroborate," *Structural Chemistry*, vol. 24, no. 2, pp. 507–515, 2013
59. O. Castellano, R. Gimon, and H. Soscun, "Theoretical study of the σ-π and π-π interactions in heteroaromatic monocyclic molecular complexes of benzene, pyridine, and thiophene dimers: implications on the resin-asphaltene stability in crude oil," *Energy and Fuels*, vol. 25, no. 6, pp. 2526–2541, 2011.
60. R. Anantharaj and T. Banerjee, "Quantum chemical studies on the simultaneous interaction of thiophene and pyridine with ionic liquid," *AIChE Journal*, vol. 57, no. 3, pp. 749–764, 2011.
61. Donati GL, Nascentes CC, Nogueira ARA, Arruda MA, Nóbrega JA. Acid extraction and cloud point preconcentration as sample preparation strategies for cobalt determination in biological materials by thermospray flame furnace atomic absorption spectrometry. Microchemical Journal. 2006;82(2):189-95.
62. Giokas D, Paleologos E, Tzouwara-Karayanni S, Karayannis M. Single-sample cloud point determination of iron, cobalt and nickel by flow injection analysis flame atomic absorption spectrometry—application to real samples and certified reference materials. Journal of Analytical Atomic Spectrometry. 2001;16(5):521-6.
63. Safavi A, Abdollahi H, Nezhad MH, Kamali R. Cloud point extraction, preconcentration and simultaneous spectrophotometric determination of nickel and cobalt in water samples. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2004;60(12):2897-901.
64. Lemos VA, da França RS, Moreira BO. Cloud point extraction for Co and Ni determination in water samples by flame atomic absorption spectrometry. Separation and Purification Technology. 2007;54(3):349-54.
65. Tong S, Jia Q, Song N, Zhou W, Duan T, Bao C. Determination of gold (III) and palladium (II) in mine samples by cloud point extraction preconcentration coupled with flame atomic absorption spectrometry. Microchimica Acta. 2011;172(1):95-102.
66. Yu F, Xi C, He Z, Chen L. Development of cloud point extraction for simultaneous extraction and determination of platinum and palladium using inductively coupled plasma optical emission spectrometry in platinum-palladium spent catalysts. Analytical letters. 2010;43(6):972-82.
67. Shokoufi N, Shemirani F, Shokoufi M. Laser induced-thermal lens spectrometry after cloud point extraction for the determination of trace amounts of palladium. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2009;74(3):761-6.