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Sequential extraction of platinum, cisplatin and carboplatin from environmental samples and pre-concentration/separation using vesicular coacervative extraction and determination by continuum source ETAAS

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ABSTRACT

A sequential extraction procedure is developed for the separation of trace levels of hexachloroplatinate, cisplatin and carboplatin from soil, which are then, pre-concentrated using a vesicular coacervative cloud point extraction method prior to their determination as platinum by continuum source ETAAS. Sequential extraction of carboplatin, cisplatin and hexachloroplatinate from a specific red soil is achieved by using the 20% HCl, aqua regia at room temperature and by combination of aqua regia and HF with microwave digestion, respectively. The pre-concentration of these species from the extracted solutions is based on the formation of extractable hydrophobic complexes of $PtCl_6^{2-}$ anionic species with free cationic head groups solubilizing sites of the Triton X-114 co-surfactant stabilized TOMAC (tri-octyl methyl ammonium chloride) vesicles through electrostatic attraction. This process separates the platinum from bulk aqueous solution into a small vesicular rich phase. The parameters affecting the extraction procedures are optimized. Under the optimized conditions, the achieved pre-concentration factor is 20 and detection limit is 0.5 ng g^{-1} for soil and 0.02 ng mL^{-1} for water samples. The spiked recoveries of hexachloroplatinate, cisplatin and carboplatin in water and soil extracts in the vesicular coacervative extraction are in the range of 96–102% at 0.5–1 ng mL^{-1} with relative standard deviation of 1–3%. The accuracy of the method for platinum determination is evaluated by analyzing CCRMP PTC-1a copper–nickel sulfide concentrate and BCR 723 road dust certified reference materials and the obtained results agreed with the certified values with 95% confidence level of student *t*-test. The results were also compared to mixed-micelle (MM)-CPE method reported in the literature [22].

1. Introduction

Platinum is a rare element, however, its use has increased in recent years and is grouped among the most precious metals [1]. The consumption of platinum is in ornaments and jewelry and in different industries like automobiles in catalytic exhaust gas converters, chemicals, petrochemicals, electrical, glass and aircraft manufacturing [2]. Some of its compounds are used as medicine in chemotherapy treatment and drug delivery [3,4]. Thus, there are many sources through which platinum can enter into the environment. Platinum as metal is not considered as toxic as for example lead, but its salts/drugs do cause changes in DNA and is therefore hazardous to health [5]. It has been reported that most of the platinum based drugs administered to the cancer patient comes out intact, through renal route, and can contaminate the surrounding water and soil [6,7]. Therefore, there is a growing interest in the determination of platinum and its cancerostatic species such as cisplatin and carboplatin in biological and environmental matrices [8–10]. In biological matrices platinum speciation is needed to understand their therapeutic action in cancer treatment, while in environmental matrices more concern is focused on its stability and interaction with soil and water. Capillary electrophoresis and reversed phase high performance liquid chromatography coupled to ICP-MS have been used for platinum speciation in aqueous extracts of platinum treated soil [11]. Ion exchange chromatography coupled to ICP-AES and ICP-MS have been used for speciation of inorganic platinum chloride complexes spiked to soil and road dust, respectively [11,12]. It seems that platinum when present as $PtCl_6^{2-}$ is more strongly attached to the soil matrix than $PtCl_4^{2-}$ and requires combination of hydrochloric, nitric and hydrofluoric acids to extract. There are only few publications of direct separation of cisplatin and carboplatin form soil, where these have been separated by using chromatographic methods [13], no work to the best of our knowledge is available in literature where non-chromatographic

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sequential separation of platinum, cisplatin and carboplatin has been achieved from any specific soil and subsequently pre-concentrated using cloud point extraction method prior to continuum source ETAAS determination.

Since last three decades large number of cloud point extraction (CPE) methods have been developed for the determination of inorganic trace and ultra trace analytes [14–16], where nonionic micelles are used, but only few are reported for platinum [17–22]. Recently, ionic micelles have been used in combination with electrolytes and co-surfactant for the determination of organic pollutants and bulky hydrophilic ionic analytes [23–27]. However, these coacervative extraction procedures have not yet been applied to extraction of platinum, because the presence of electrolytes reduces the ionic micelles extraction efficiencies by neutralizing the useful reactive head group solubilizing sites.

The aim of our work is to investigate the potential Pt species presented in the soil samples which are mainly obtained from automobile catalytic converters emissions and cancer hospital wastes and to develop a method for their separation and extraction. The possible species could be Pt (IV) and Pt (II). For Pt (IV) we used hexachloroplatinate, and for Pt (II) two species Carboplatin and Cisplatin was used which has its origin from hospital waste. For the first time, in this work, we describe a sequential extraction method using combination of acids to separate inorganic Pt (IV), cisplatin and carboplatin from a specific red soil and then pre-concentrate them using a vesicular coacervative cloud point extraction (VC-CPE) method. Tri-octyl methyl ammonium chloride (TOMAC) vesicles are formed by addition of Triton X-114 to TOMAC. The pre-concentration of hexachloroplatinate is based on the formation of extractable hydrophobic complexes of $PtCl_6^{2-}$ with free cationic head groups solubilizing sites TOMAC vesicles through electrostatic attraction. The accuracy of this method for platinum determination is verified by analyzing certified reference materials such as CCRMP PTC-1a copper–nickel sulfide concentrate and BCR 723 road dust and speciation results are validated by using spike recovery study because no certified reference material are available for cisplatin and carboplatin. This procedure is then applied to pre-concentration and separation of hexachloroplatinate, cisplatin and carboplatin from red soil samples. It has also been used to separate hexachloroplatinate and cisplatin+carboplatin (cancerostatic compounds) together from water samples. The pre-concentrated species are then determined by continuum source ETAAS. Small angle neutron scattering (SANS) has been used to prove the formation of vesicles by addition of Triton X-114 to TOMAC.

2. Experimental

2.1. Instrumentation

Hexachloroplatinate concentrations in the dissolved vesicular rich phases were determined by using continuum source ETAAS (Contra AA 700, Analytik Jena AG, Jena, Germany). A transversely heated graphite tube, MPE 60 auto sampler and xenon short arc lamp in hot-spot mode operated at 300 W as a continuum radiation source were used. A high resolution double monochromator consisting of a prism and an echelle grating monochromator, providing a spectral bandwidth per pixel of ca. 2 pm at 200 nm was used. A linear charge coupled device array detector total 588 pixels, out of which 200 pixels were used for the determination of dispersed radiation. The platinum absorption was measured using the central pixel (CP) ± 1 pixels. Argon with a purity of 99.99% was used as the purge gas in all stages, except during atomization step. A spectral line at 265.9450 nm was used. The optimized temperature program used for the determination of the platinum is given in Table 1. All samples were digested using a MARS (CEM, Matthews, NC, USA) microwave oven and PTFE vessels. Small angle neutron scattering (SANS) experiments were performed at the Dhruva reactor, BARC, Mumbai, India [28]. The incident neutron beam (λ=5.2 Å) was used. The scattered neutron cross-sections ($d\Sigma/d\Omega$) were measured using a linear He^3 position sensitive detector. All the matrices were digested in high pressure 1500 Teflon vessels using a MARS (CEM, Matthews, NC, USA) microwave digester equipped with temperature and pressure sensors. Rotary mixer (Tarsons, Kolkata, India) was used for mixing the soil samples with extracting acids.

Table 1
Optimized temperature program used for the determination of platinum in the vesicular rich phase after vesicular coacervative cloud point extraction using continuum source ETAAS.

Step	Temperature (°C)	Ramp (°C s^{-1})	Hold (s)	Ar flow (mL min^{-1})
Drying-1	80	6	20	250
Drying-2	90	3	20	250
Drying-3	110	5	10	250
Pyrolysis	1200	300	10	250
Gas adaption	1200	0	5	250
Atomization	2300	1000	4	0 (read)
Cleaning	2400	500	3	250

2.2. Reagents and standard solutions

Ultra pure water (18.2 MΩ cm) obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used to prepare all the solutions. Acids such as HCl and HNO_3 procured analytical grade from Merck, Darmstadt, Germany, which are further purified using a sub-boiling distillation system made up of quartz. Suprapur grade HF was used. The individual surfactant solutions of 10% m/v Triton X-114 in water and TOMAC in methanol (Sigma-Aldrich, Steinheim, Germany) were prepared by taking 1 g of these surfactants in to 10 mL of water and methanol. Pt(IV) stock solution (1 mg mL^{-1}) was prepared by dissolving the metal (99.9% Johnson Matthey, West Chester, USA) in minimum amount of aqua regia and evaporated to near dryness and finally taken up in 10% v/v HCl. The stock solution of 1 mg mL^{-1} cisplatin and carboplatin (Pfizer, Bentlay WA, Australia) was used for spiking the soil and water samples and calculated as elemental platinum. The working standards were prepared by subsequent dilutions of stocks. Methanol (analytical grade, Merck, Darmstadt, Germany) was used for dissolving the vesicular rich phases. Stock standard solutions (1 mg mL^{-1}) of analytes such as Mg^{2+}, Ca^{2+}, Cu^{2+}, Ni^{2+}, Ag^{1+}, Pb^{2+}, Fe^{3+} and Co^{2+} (Merck, Darmstadt, Germany) chloride salts and SO_4^{2-} and PO_4^{3-} (Merck, Darmstadt, Germany) sodium salts of analytical grades were used for interference study. The surface red soil sample 1 and sample 2 were collected in rural and urban areas in and around the metropolitan city, Hyderabad, India during winter season. These soil samples were ground and sieved though the 100 μm nylon sieves and used for the extraction of platinum species. Soil sample 1 was used for measuring the pH, cationic and anionic exchange capacity, redox potential, carbon and nitrogen contents and the results are shown in Table 2. This sample was digested in microwave using aqua regia and used for determination cations using ICP-OES. Anions in this soil sample were determined using IC after water extraction. The certified reference materials analyzed in this method were CCRMP PTC-1a copper–nickel sulfide concentrate and BCR 723 road dust.

2.3. Synthesis of spiked soil and water samples

Accurately weighted 1 g of sample 1 in five cleaned PTFE Petri dishes and spiked in the range of 1–2 μg of hexachloroplatinate, cisplatin, carboplatin and their mixture to each sample aliquot. These samples were air dried inside the clean bench for 48 h. These dried samples were further homogenized using motor and piston and then used for sequential extraction of spiked species. Water samples were spiked in the range of 0.5–1 ng mL^{-1} of hexachloroplatinate, cisplatin and carboplatin and their mixture equilibrated at room temperature for 1 h before the extraction.

Table 2
Characterization of the soil sample (sample 1) used in the extraction of platinum species.

Type of soil	Red soil
Initial soil pH	8.1
Cation-exchange capacity (mM g^{-1})	9.50
Anion-exchange capacity (mM g^{-1})	4.97
Redox potential (mV)	375
Organic carbon (%)	0.6 ± 0.02
Total organic matter (%)	1.03 ± 0.03
Nitrogen (kg ha^{-1})	410 ± 130
Analytes	Measured concentration (μg g^{-1})
Ca^{2+}	6480 ± 60
Mg^{2+}	4650 ± 80
Fe^{3+}	28540 ± 30
Al^{3+}	29680 ± 40
Na^{+}	540 ± 20
Mn^{2+}	260 ± 30
P^{5+}	47.57 ± 0.55
Pb^{2+}	44.86 ± 0.62
Cu^{2+}	22.2 ± 0.76
Cd^{2+}	5.64 ± 0.58
SO_4^{-2}	22.8 ± 0.48
NO_3^{-}	8.7 ± 0.36
Cl^{-}	5.5 ± 0.24
F^{-}	0.95 ± 0.09

2.3.1. Sequential extraction of individual species of platinum from soil matrix

The inorganic Pt (IV), cisplatin, carboplatin and total platinum were separated sequentially from soils using the scheme shown in Fig. 1, which is described as follows:

2.3.1.1. Extraction of carboplatin. About 100–200 mg of spiked and un-spiked soil samples were accurately weighted and transferred into pre-cleaned polypropylene centrifuge tubes of 15 mL size with screw cap. To this 5 mL of 20% v/v HCl was added and mixed well at room temperature using rotary mixture operated at 25 rpm for 30 min and centrifuged. The carboplatin was selectively extracted in to the supernatant and separated residual soil was washed with same quantity of HCl to separate the residual carboplatin immediately and added to first extract.

2.3.1.2. Extraction of cisplatin. To the above residual soil, 3 mL aqua regia (3:1 M ratio, HCl:HNO_3) was added, made up to 5 mL and was mixed well at room temperature using rotary mixture operated at 25 rpm for 60 min and centrifuged. The cisplatin was selectively separated from residual soil into the supernatant and inorganic platinum was left in the remaining residual soil. It was washed with same quantity of aqua regia to separate the residual cisplatin and added to first extract.

2.3.1.3. Extraction of residual hexachloroplatinate or total platinum from soil using aqua regia. About 200–400 mg of certified reference material, un-spiked and spiked soil samples, residual soil obtained after extraction of cisplatin and carboplatin were treated with mixture of 4 mL aqua regia and 1 mL HF in a pre-cleaned high pressure Teflon vessels and the extracts (supernatant) of cisplatin and carboplatin were digested in the same type of Teflon vessels using an optimized microwave temperature program: 220 °C for 15 min at 800 psi. This heating program was repeated twice for complete digestion and conversion of all platinum species into inorganic platinum. These solutions were evaporated to near dryness and the final residue was

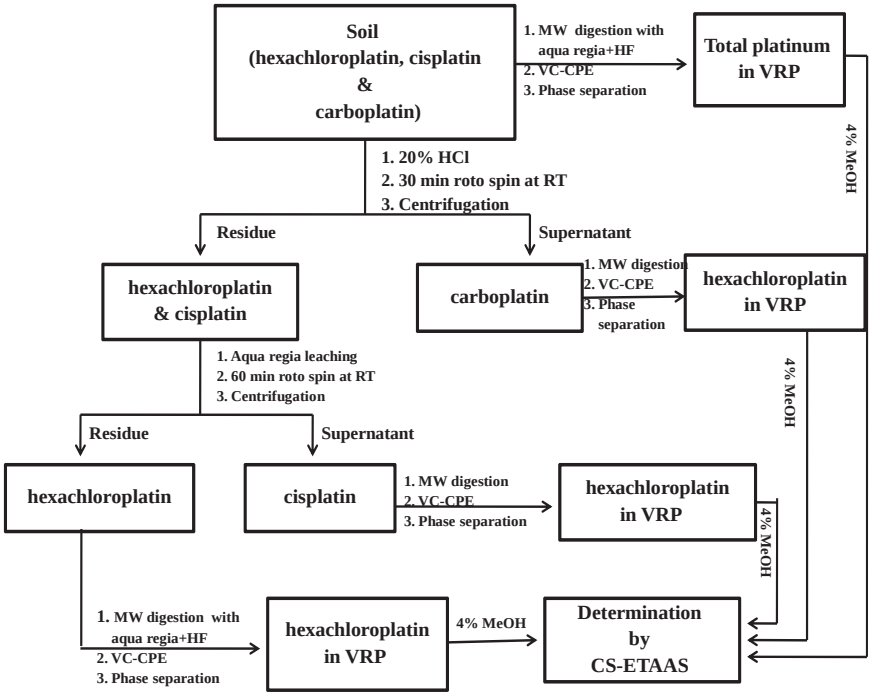

Fig. 1. Scheme of sequential separation and pre-concentration of carboplatin, cisplatin, hexachloroplatinate and total platinum from the soil matrices using selective extracting acids followed by using proposed VC-CPE method.

dissolved in 1 mL HCl and made up to 10 mL with Milli-Q water. The pre-concentration of hexachloroplatinate from these digests was carried out using procedure described -in Section 2.4. Procedural blanks were also prepared in the similar manner.

2.3.2. Separation of inorganic Pt (IV) and (cis+carbo) platins together from water matrix

The inorganic Pt (IV) and (cis+carbo) platins were separated from water using the following sequence as shown in Fig. 2.

2.3.2.1. Extraction of inorganic Pt (IV). About 5–10 mL spiked and un-spiked water samples were transferred into pre-cleaned centrifuge tubes with screw cap of 15 mL size and added 0.5 mL HCl and then used the VC-CPE procedure described in Section 2.4. This extraction procedure selectively separates and pre-concentrates the inorganic Pt (IV) from the aqueous mixture of inorganic Pt (IV) and (cis+carbo) platins into vesicular rich phase. The supernatant contains the (cis+carbo) platins.

2.3.2.2. Extraction of (cis+carbo) platins together. The above supernatant containing (cis+carbo) platins were converted into anionic chloro complexes together using above mentioned microwave digestion procedure and then used the VC-CPE procedure mentioned in Section 2.4.

2.4. Vesicular coacervative cloud point extraction procedure

Aliquots of 2–5 mL digested matrices were taken in polypropylene centrifuge tubes and adjusted the HCl concentration to 5% v/v and then 1 mL of 10% m/v TOMAC and 0.5 mL of 10% m/v Triton X-114 were added and made up to 20 mL using Milli-Q water. The solutions were mixed well and left at room temperature. After 20 min, a small volume of vesicular rich phase accumulated on the top of the aqueous solution, which was separated using a micropipette. The viscosity of the vesicular rich phase was reduced by dissolving it with 1 mL methanol and was analyzed for platinum using CS-ETAAS. Procedural blanks were also prepared in a similar manner.

3. Results and discussion

3.1. Selective extraction inorganic Pt (IV), cisplatin and carboplatin from soils

Most of the platinum compounds are found to be stable in hydrochloric acid, this medium was studied first to extract inorganic Pt (IV), cisplatin and carboplatin from soil samples that were spiked with these species separately in the range 1–2 $\mu g\ g^{-1}$. Since in dissolved aqua regia Pt(IV) exist as hexachloroplatinate, hence it has been used as surrogate for inorganic Pt (IV) in the manuscript. Further, the levels of these species were high, it were directly determined without applying VC-CPE. Fig. 3 shows the extraction efficiencies of these species from spiked soil with 5 mL of 0–30% v/v HCl. These results indicate that with increase in concentration of HCl, there is a gradual increase in extraction of carboplatin and is almost 100% when concentration of HCl is 15–30%. Hexachloroplatinate and cisplatin, on the other hand is not extracted at all in 0–5% HCl and only 1–5% extraction was observed, even when HCl concentration used was as high as 30%. To extract carboplatin selectively, 5 mL of 20% v/v HCl was selected. It appears that both hexachloroplatinate and cisplatin upon addition to soil formed strong bonds with silicate matrix and therefore not extracted with HCl alone.

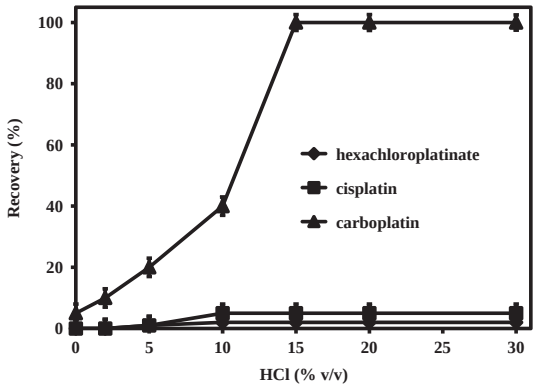

Fig. 3. Selective separation of carboplatin from spiked soil samples in presence of cisplatin and hexachloroplatinate with varying concentrations of HCl. The error bars indicate the relative standard deviation at each measurement ($n=3$).

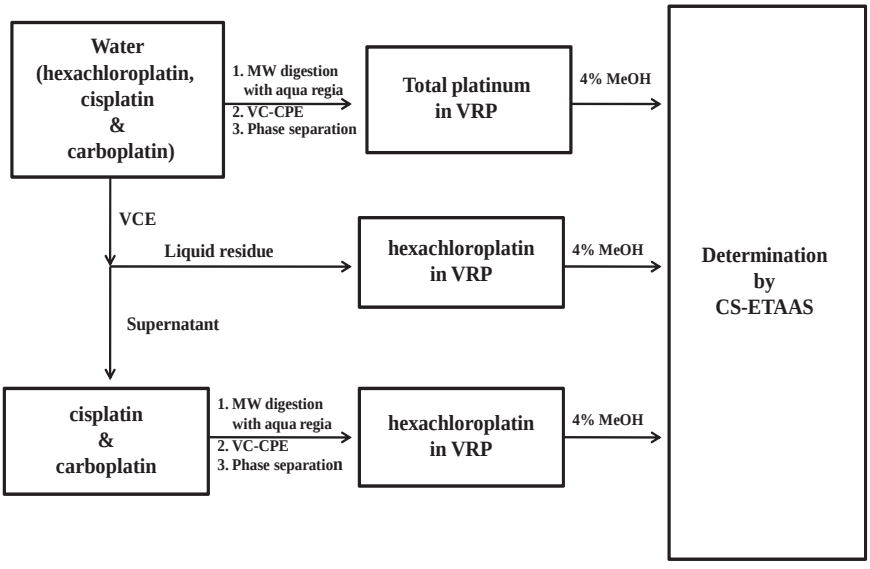

Fig. 2. Scheme of selective separation and pre-concentration of hexachloroplatinate, total platinum and together cisplatin and carboplatin from water matrices using proposed VC-CPE method.

In order to separate hexachloroplatinate and cisplatin from the residual soil, aqua regia, 3:1 M mixture of HCl and HNO_3 made up to 5 mL was used. These samples were rotary mixed at 25 rpm in the extraction time intervals between 0.5 and 48 h and the extraction efficiencies of hexachloroplatinate and cisplatin are shown in Fig. 4. These results indicated that with increase in the extraction time from 0.5 to 1 h, the extraction efficiency of cisplatin increased from 55% to 75%. When the extraction time was increased from 1 to 48 h, then the extraction efficiency increased from 75% to 80%. Hexachloroplatinate on the other hand showed only 2–5% extraction efficiency between 0.5 and 1 h period, which gradually increased to a maximum of 10% after 48 h extraction time. Hence, to extract cisplatin selectively from the mixture of cisplatin and hexachloroplatinate spiked residue, 1 h extraction time was selected. In case, an excess of hexachloroplatinate is present, a cross sensitivity of 5% can interfere in the determination of cis- and carboplatin extraction. This can be corrected by carrying out VC-CPE procedure without applying microwave digestion, where only hexachloroplatinate is extracted (Section 3.7).

To extract hexachloroplatinate quantitatively from soil matrices microwave treatment was needed after addition of aqua regia and HF to the sample. It is observed that from the spiked soil, it is easier to extract carboplatin, but more stringent treatment is needed to extract cisplatin and hexachloroplatinate. These extraction efficiencies mainly depend on the bond formation capacity of chloride ligands, oxidation state and its exchange capacity with silicate matrix as stated in the literature [11].

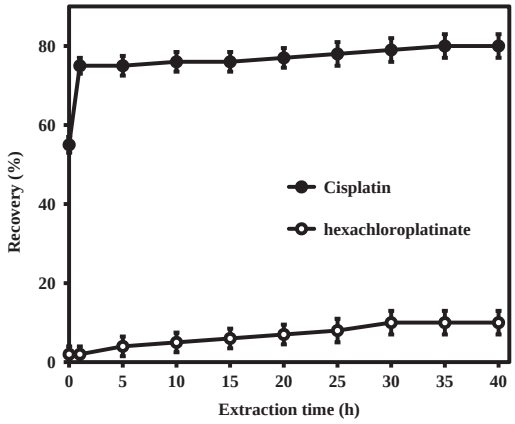

Fig. 4. Variation of recovery (%) of cisplatin and hexachloroplatinate from residual soil with extraction time using aqua regia at room temperature. The error bars indicate the relative standard deviation at each measurement ($n=3$).

Table 3 shows the results of recovery study carried with spiked platinum species in soil. These results indicated that these recoveries were in the range of 97–99, 77–80, and 96–110, respectively for carboplatin, cisplatin and hexachloroplatinate. The recovery of total platinum which includes hexachloroplatinate, cisplatin and carboplatin was found to be in the range of 97–100%. The relative standard deviation was in the range of 1–4%. These results showed that the separation of carboplatin, cisplatin and hexachloroplatinate were possible from the soil matrices. Even though it appears that the separation of cisplatin is not quantitative, it is useful to ascertain the presence of extractable carcinogen such as cisplatin.

3.2. Optimization of vesicular coacervative cloud point extraction parameters

The vesicular coacervative phase separation has been achieved by introducing the concept of increasing the hydrophobic character of TOMAC ionic aggregates, by addition of nonionic Triton X-114 co-surfactant, without neutralizing the reactive head group solubilizing sites. These free reactive head groups are used for electrostatic extraction of hexachloroplatinate in the hydrochloric acid medium. It is well known that platinum form stable anionic species with chloride ions mostly anionic hexachloroplatinate $PtCl_6^{2-}$, which react electrostatically with cationic TOMAC vesicles stabilized by nonionic Triton X-114 surfactant. Therefore various parameters affecting the extraction efficiency were studied.

3.2.1. Effect of acid concentrations

Since HCl and a mixture of HCl and HNO_3 is used for extraction of hexachloroplatinate, hence, the effect of HCl and combined effect of HCl and HNO_3 mixtures on the recoveries of hexachloroplatinate were studied in the range 1–30% v/v using vesicular coacervative extraction and the results are shown in Fig. 5. Initially, the effect of only HCl was studied. As shown in Fig. 5, in the studied concentrations range, the recoveries of hexachloroplatinate were with-in 98–102% range. The uniform recovery of hexachloroplatinate indicates the high reactivity of the charged head groups of the vesicles. It is mainly due to availability of the large number of free charged vesicular head groups, which are stabilized by co-surfactant. Hence, 5% v/v HCl was selected for further studying the effect of HNO_3. The recovery of hexachloroplatinate was nearly 90–100% up to 15% v/v nitric acid but reduced to 75%, when its concentration was increased to 30%. This indicates that at higher concentrations of HNO_3, the reactivity of

Table 3
Sequential selective extraction efficiency of hexachloroplatinate (Pt^{+4}), cisplatin, carboplatin and total platinum from soil sample 1 using selective acids as shown in Fig. 1.

Amount spiked (ng g^{-1})			Found[a] (ng g^{-1}) (Recovery, %)[b]			
Pt^{+4}	Cisplatin	Carboplatin	Pt^{+4}[c]	Cisplatin[d]	Carboplatin[e]	Total platinum[f]
1500	0	0	1440 ± 45 (96 ± 3)	ND[g]	ND[g]	1455 ± 60 (97 ± 4)
0	2000	0	360 ± 40 (18 ± 2)	1600 ± 40 (80 ± 2)	ND[g]	1980 ± 60 (99 ± 3)
0	0	2000	ND[g]	ND[g]	1960 ± 40 (98 ± 2)	1980 ± 60 (99 ± 3)
1000	1000	0	1110 ± 40 (111 ± 4)	820 ± 30 (82 ± 3)	ND[g]	1940 ± 20 (97 ± 1)
1000	0	1000	980 ± 20 (98 ± 2)	ND[g]	990 ± 20 (99 ± 2)	1980 ± 10 (99 ± 1)
1000	1000	1000	1080 ± 40 (108 ± 4)	810 ± 30 (81 ± 3)	980 ± 20 (98 ± 2)	2970 ± 20 (99 ± 2)

[a] Values were means of four measurements ± standard deviation.
[b] Values in parenthesis indicates the recoveries.
[c] Values were obtained from residual soil after microwave digestion with aqua regia and HF.
[d] Values were obtained from room temperature aqua regia leaching of the residual soil.
[e] Values were obtained from room temperature 20% HCl leaching of the soil.
[f] Values were obtained by applying microwave digestion with aqua regia and HF on a fresh soil aliquot.
[g] Not detected.

the active interacting sites was affected, which reduces the recoveries. Therefore, in the presence of 5% HCl the maximum tolerable concentration of HNO_3 was 15%. However, the microwave digested solutions were evaporated to near dryness and the final residue was dissolved in 10% HCl, hence, this procedure can easily be applied to these solutions.

3.2.2. Effect of TOMAC and Triton X-114 concentration

The optimization of TOMAC and Triton X-114 concentration is necessary because the electrostatic extraction efficiency of cationic vesicles depends up on the surface charge density of reactive head group solubilizing sites of the extracting TOMAC and Triton X-114 aggregates. However, at first the morphological changes, during the phase separation of 0.5% m/v TOMAC, 2% m/v Triton X-114 and their mixture were studied using SANS because additives such as electrolytes and co-surfactants are adsorbed at different regions of ionic aggregates that vary the size and shape of final aggregates [29]. The results are shown in Fig. 6. From this it is observed that TOMAC alone forms fine vesicular aggregates that are unable to separate because of its fast disintegration; on the other hand Triton X-114 alone has shown the formation of stable micelles. Addition of 1% Triton X-114 to 0.5% TOMAC indicates the formation of vesicles by stabilization of fine TOMAC aggregates with Triton X-114. However, by increase in the concentration of Triton X-114 further to 2% shows the conversion of some of the vesicles into mixed-micelles. This information was used to select the range for optimizing TOMAC and Triton X-114 concentrations. Their concentrations were optimized in the range of 0–1.7% m/v and results are shown in Fig. 7. In the absence of TOMAC, it is observed that

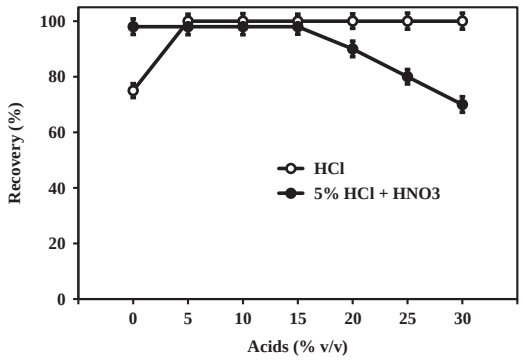

Fig. 5. Effect of acids on the recovery of hexachloroplatinate in the proposed room temperature vesicular coacervative cloud point extraction method. The fixed parameters are 0.5% m/v TOMAC, 0.25% m/v Triton X-114. The error bars indicate the relative standard deviation at each measurement ($n=3$).

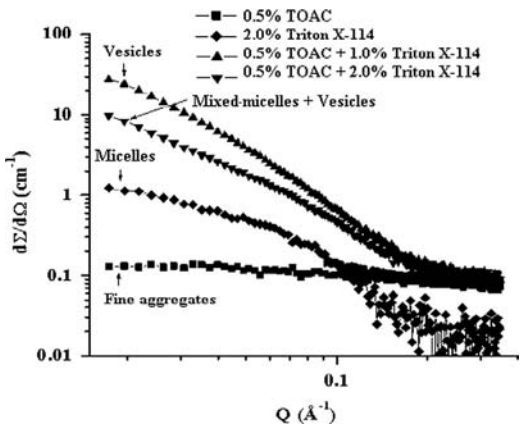

Fig. 6. Variation of TOMAC morphology with Triton X-114 co-surfactant with small angle neutron scattering (SANS).

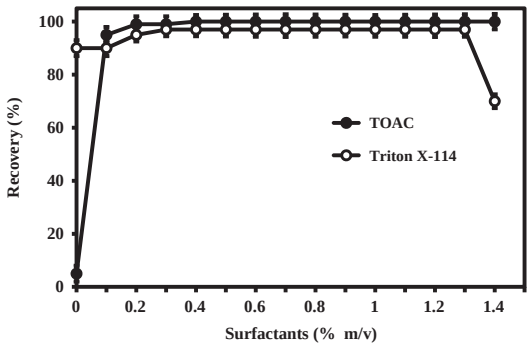

Fig. 7. Effect of TOMAC and Triton X-114 surfactants concentration on the recovery of hexachloroplatinate in the proposed room temperature vesicular coacervative cloud point extraction. Conditions for TOMAC optimization: 5% v/v HCl and 0.25% m/v Triton X-114. Conditions for Triton X-114 optimization: 5% v/v HCl and 0.5% m/v TOMAC. The error bars indicate the relative standard deviation at each measurement ($n=3$).

the clouding system acts as a nonionic surfactant based cloud point extraction, therefore only 5% recovery of platinum was obtained, but when TOMAC is added in the range of 0.1–1.7%, the corresponding recovery increased to 99–103% range. This indicates the formation vesicles with high surface charge density. However, at 0.1% TOMAC, the formed vesicular rich phase was very small (50 μL) that affected the precision which was 5–8%. When the concentration of TOMAC was between 0.3% and .5% good precision of 1–3% was obtained, 0.5% TOMAC was used for this work.

Similar study was carried out using Triton X-114. Without Triton X-114, coacervative phase separation was observed but only small vesicle aggregates (as shown in Fig. 6) were formed, which made the phase separation difficult. The TOMAC aggregates were stabilized by addition of Triton X-114 in the range 0.1–1.5% and the recoveries obtained were between 99% and 103% with the precision of 1.5–2.5%. Further increase in Triton X-114 concentration to 1.7% caused the conversion of vesicles in to mixed-micelles (as shown in Fig. 6) and reduced the recovery to 70%. Hence, 0.25% m/v Triton X-114 was selected.

3.2.3. Effect of incubation temperature and time

Hexachloroplatinate is a d^6 ion and its participation in chemical reaction is slow compared to d^8 tetrachloroplatinate. This kinetic inertness was confirmed in recent report of cloud point extraction using chelating agent [18,19]. The rate of reaction of d^6 platinum can be improved by increasing the temperature of solution. Most of the reported cloud point extraction systems indicated that the higher incubation temperature provides better removal of water from micelle aggregates and provides a smaller volume of surfactant rich phase, which consequently increase the pre-concentration factor. Hence, the effect of incubation temperature was studied. The selected incubation temperature must be higher than the cloud point temperature of the clouding solution. The clouding temperature of the TOMAC and Triton X-114 solution was 5 °C. Therefore, the effect of incubation temperature was studied in the range of 25–90 °C, using 60 min incubation time, on initial vesicular rich phase volume, and pre-concentration factors (PCF).

The PCF is the ratio of the analyte concentration in the final volume of vesicular rich phase to that of the initial aqueous phase. The results showed that the volume of vesicular rich phase formed is constant when incubation temperature is varied from 25 to 90 °C. It indicates that the vesicles formed are highly hydrophobic and no water molecules are bounded to vesicular aggregates even at room temperature (25 °C), like surfactant rich phase obtained in the case of nonionic surfactant based CPE. This behavior is quite

different than that from a nonionic surfactant based cloud point extraction system and provided PCF of 20 in all studied incubation temperatures. Therefore, room temperature incubation temperature was selected for studying the effect of incubation time. The optimization of incubation time was carried out in between 10–120 min. These results show that extraction of platinum is fast and showed 95–101% recoveries in all studied time intervals in proposed procedure. Hence, a 20 min incubation time was selected.

3.3. Interferences studies

In order to evaluate the suitability of this procedure to different environmental matrices, the highest tolerability of various common interfering ions was studied. The highest tolerability of various foreign ions spiked with 2 ng mL^{-1} hexachloroplatinate, by keeping the relative error between $\pm 5\%$ were found to be 300 mg L^{-1} of Mg^{2+}; 200 mg L^{-1} of Ca^{2+}; 100 mg L^{-1} of Cu^{2+}, Ni^{2+}, Ag^{1+} and Pb^{2+}; 50 mg L^{-1} of Fe^{3+}; 10 mg L^{-1} of Co^{2+}; 2 mg L^{-1} of SO_4^{2-} and 3 mg L^{-1} of PO_4^{3-} for proposed VC-CPE.. Therefore, these results demonstrated the high selectivity of the proposed process for the extraction of anionic hexachloroplatinate.

3.4. Optimization of furnace temperature program

Optimization of furnace temperature program is necessary for the determination of platinum using ETAAS. Hence, the effect of pyrolysis and atomization temperatures on the absorbance signal of 10 ng mL^{-1} of platinum before and after pre-concentration using the proposed VC-CPE was studied and these results are shown in Fig. 8. The higher signal after extraction is due to pre-concentration (about 20 times) of the hexachloroplatinate in the organic phase. These results indicated that the integrated absorbance values increased by increase in the pyrolysis temperature from 800 to 1000 °C and then reached the plateau region between 1100 and 1500 °C. Further increase in the pyrolysis temperature causes decrease in the absorbance signal. Hence, a 1200 °C pyrolysis temperature was selected and then optimized atomization temperature in the range of 2000–2400 °C. These results indicated that the absorbance values increased by increase in the atomization temperature up to 2200 °C and then reached a plateau. Hence, a 2300 °C atomization was selected. Same behavior of hexachloroplatinate in aqueous standard and vesicular rich phase indicates absence of matrix effects.

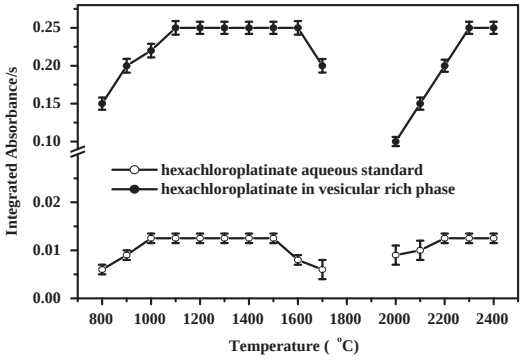

Fig. 8. Effect of pyrolysis and atomization temperature on the absorbance of 10 ng mL^{-1} of platinum in 0.2% HNO_3 and vesicular rich phase. The error bars indicate the relative standard deviation at each measurement ($n=3$).

3.5. Analytical figures of merit

Under the optimized experimental conditions, the calibration curves were obtained by pre-concentrating the successively spiked standards of platinum in the range of 0.2–40 ng mL^{-1} for VC-CPE. The correlation coefficient was 0.9995, indicating the good linearity. Quantifications have been performed by external calibration using aqueous standards prepared in 0.2% HNO_3. The limit of detection calculated based on three times the standard deviation of ten measurements of procedural blanks was 0.5 ng g^{-1} for soil and 0.02 ng mL^{-1} for water samples. The advantages of the proposed procedure were comparable with the recently published nonionic surfactant and mixed-micelle based CPE [18–23]. It clearly shows the utility of active head group solubilizing sites of vesicles that act as an internal chelating agent and avoid the addition of external chelates and it also avoids the use of higher incubation temperatures (>90 °C) and a prolonged heating time (120 min) used in the nonionic surfactant based CPE for the quantitative extraction of platinum [19,20]. However, the temperature independence formation of vesicular rich phase is one of the added advantages compared to nonionic based CPE and MM-CPE [22,23].

3.6. Validation of the method for determination of platinum

Due to unavailability of soil and water certified for these platinum species, the accuracy of the proposed vesicular coacervative cloud point extraction was validated by using CCRMP PTC-1a copper–nickel sulfide (ore) and BCR 723 road dust certified reference materials certified for total platinum and the results were cross validated with an alternative method reported in the literature using MM-CPE [22]. The results of two soil samples along with the certified reference material are given in Table 4. The values obtained are in good agreement with certified value based on student t-test at 95% confidence level and compares well with the alternate procedure. The accuracy of the cisplatin and carboplatin separation and pre-concentrations were validated by using the spike recovery study because no certified reference materials are available.

Table 4
Analytical results of total platinum determined in the certified reference materials and real soil samples using CS-ETAAS after vesicular coacervative cloud point extraction.

Matrices	**Measured values** (ng g^{-1}) (mean $\pm$ [a] $ts(n-1)^{-1/2}$)		Certified value (ng g^{-1})
	Proposed VCE	Reported MM-CPE[b]	
PTC-1a copper–nickel sulfide concentrate[c]	2.74 ± 0.13	2.78 ± 0.14	2.72 ± 0.11
BCR 723 road dust	80.6 ± 1.8	82.2 ± 2.8	81.3 ± 3.3
Soil sample 1	31 ± 4	30 ± 4	–
Soil sample 2	45 ± 5	44 ± 3	–

[a] $t_{0.95}=3.18$, $n=4$ (Four measurements) and s=standard deviation.
[b] Mixed-micelle cloud point extraction [22].
[c] Values are in μg g^{-1}.

Table 5
Vesicular coacervative cloud point extraction recoveries of hexachloroplatinate (Pt^{4+}), (cis+carbo) platins and total platinum from selective sequential extracts of water samples using the scheme given in Fig. 2.

Amount spiked (ng mL^{-1})			Recovery [a] (%)		
Pt^{+4}	Cisplatin	Carboplatin	Pt^{+4}	(cis+carbo) Platins[b]	Total platinum
Water					
0.5	0	0	98 ± 3	ND[c]	99 ± 3
0	0.5	0	ND[c]	96 ± 2	100 ± 3
0	0	0.5	ND[c]	102 ± 3	101 ± 2
0.8	0.8	0	98 ± 2	97 ± 2	102 ± 3
1.0	0	1.0	98 ± 2	98 ± 4	101 ± 2
0.5	0.5	0.5	103 ± 3	99 ± 3	100 ± 3

[a] Values were means of four measurements ± standard deviation.
[b] Together cisplatin and carboplatin.
[c] Not detected.

Table 6
Vesicular coacervative cloud point extraction recoveries of hexachloroplatinate (Pt^{4+}), cisplatin, carboplatin and total platinum from selective sequential extracts of soil using the schemes given in Fig. 1.

Amount spiked/ng mL^{-1}			Recovery [a] (%)			
Pt^{+4}	Cisplatin	Carboplatin	Pt^{+4}	Cisplatin	Carboplatin	Total platinum
1	0	0	98 ± 2	ND[b]	ND[b]	98 ± 2
0	0.5	0	ND[b]	95 ± 2	ND[b]	97 ± 3
0	0	0.5	ND[b]	ND[b]	97 ± 2	98 ± 2
1	1	1	101 ± 2	97 ± 2	98 ± 3	100 ± 3

[a] Values were means of four measurements ± standard deviation.
[b] Not detected.

3.7. *Pre-concentration of platinum species from soil extracts and water using VC-CPE*

The VC-CPE method thus developed for hexachloroplatinate was applied to cisplatin and carboplatin soil extracts and cisplatin and carboplatin spiked water samples without microwave digestion. The results indicates that the lower recovery (< 1%) of cisplatin and carboplatin soil extracts and spiked water samples. This is because, the method extracts anionic hexachloroplatinate and not when present in any other form like cisplatin or carboplatin. In order to destroy organic platinum species and convert them to extractable $PtCl_6^{2-}$, the soil extracts and water samples were subjected to microwave treatment before VC-CPE was carried out. These results are indicated in Tables 5 and 6.

Based on these findings it is possible to separate hexachloroplatinate from cisplatin and carboplatin from water. At first hexachloroplatinate was extracted using VC-CPE into a vesicular rich phase, and the cisplatin and carboplatin in the supernatant is subjected to microwave treatment and then pre-concentrated together using VC-CPE as shown in Fig. 2. In the case of soil, the separation of the hexachloroplatinate species is already achieved during sequential extraction using different combinations of acids (Fig. 1), but in order to pre-concentrate, the cisplatin or carboplatin extracts were treated with microwave before using VC-CPE.

As stated above these samples were spiked with known concentration of the species, as no reference materials are available. The values of cisplatin and carboplatin were below the detection limits of the method in both soil and water. The recoveries of the species found in the mixture with known standards were satisfactory for both water (hexachloroplatinate, cisplatin+carboplatin) and soil matrices.

4. Conclusions

The developed method demonstrates the sequential extraction schemes for the extraction of hexachloroplatinate, cisplatin and carboplatin from soil and then pre-concentrated using a vesicular coacervative cloud point extraction procedure. In the case of water, hexachloroplatinate and cisplatin+carboplatin together can be separated and pre-concentrated by this procedure. The developed method will be useful in monitoring these species in the environment. It appears that the cisplatin and carboplatin are quite stable species and if exposed to the environment can be a cause of serious concern.

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