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Evaluation of ammonia buffer containing EDTA as an extractant for Cr(VI) from solid samples

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Abstract

A novel procedure for the extraction of soluble, sparingly soluble and insoluble Cr(VI) from solid samples was presented. EDTA was added to an ammonia buffer commonly used only for the extraction of soluble and sparingly soluble Cr(VI). In the course of extraction in an ultrasonic bath cations which form insoluble chromates are complexed with EDTA while Cr(VI) is transferred to the solution. A concentration of EDTA equal to 0.01 mol L^{-1} was chosen. The presence of EDTA in the extraction solution enables not only dissolution of insoluble Cr(VI) but also, as reported previously in literature, minimises oxidation of Cr(III) to Cr(VI). The extraction procedure was optimised and applied to Cr(VI) determination in the paint chips real sample. The results obtained were compared with the results obtained using two other extraction procedures. The results show that the novel extraction procedure can be used for the extraction of soluble, sparingly soluble and insoluble Cr(VI) from real solid samples.

Keywords: Insoluble chromium (VI); Extraction; Solid samples; Determination

1. Introduction

Chromium can occur in a number of oxidation states, but only Cr(III) and Cr(VI) are usually found in samples. Cr(III) compounds are considered to be essential for the maintenance of glucose, lipid and protein metabolism, while Cr(VI) compounds are known to be toxic and carcinogenic agents for a variety of organisms [1]. Because of different toxicities of these two valence states of chromium, it is necessary to determine rather Cr(VI) but not the total concentration of Cr to estimate the toxicity of the sample.

Determination of Cr(VI), especially in solid samples, is regarded as one of the most challenging speciation tasks [2] due to interconversions between Cr(VI) and Cr(III) in the course of the analytical process. The two major steps in the course of determination of Cr(VI) in solid samples are extraction and detection. The first step is the most problematic because oxidation of Cr(III), reduction of Cr(VI) or incomplete extraction of Cr(VI) are often reported.

Extraction of Cr(VI) using solution 0.28 mol L^{-1} Na_2CO_3 + 0.5 mol L^{-1} NaOH is the most commonly used procedure. The solution at temperatures about 95 °C quantitatively extracts soluble and insoluble forms of Cr(VI), but as shown in [2–5] a partial oxidation of Cr(III) is observed. Errors as much as 163% were reported due to oxidation of Cr(III) during the extraction using the above mentioned solution [2]. Quantitative recovery of Cr(VI) was reported using as the extractant a solution containing 10% Na_2CO_3 + 2% $NaHCO_3$ [6]. In this case before adding the extractant to the solid sample a phosphate buffer containing $MgSO_4$ should be added to the sample. Addition of Mg(II) minimises oxidation of Cr(III) to Cr(VI) and the influence of reductants present in the sample on the reduction of Cr(VI). This procedure was used in the present study as a comparative one. Another procedure exploits as an extractant 0.1 mol L^{-1} NaOH and sonication for 30 min at 25 °C. According to [7] the recovery of Cr(VI) using the procedure is lower as compared

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with extraction 0.28 mol L^{-1} Na_2CO_3 + 0.5 mol L^{-1} NaOH. To dissolve Cr(VI) from its insoluble salts in all the above procedures the metal ion that form insoluble chromate as e.g. Pb(II) is precipitated as hydroxide or carbonate.

Another commonly used procedure exploits an ammonium sulphate/ammonium hydroxide buffer as an extraction mixture [8–11]. In this case extraction is carried out in an ultrasonic bath at a temperature below 40 °C. Although this procedure was applied in many studies [8–11] only in [11] it was reported that the recovery for insoluble Cr(VI) is about 90%. The authors do not give detailed information about preparation of a sample containing insoluble Cr(VI) for extraction. In a more recent paper it was reported that insoluble Cr(VI) is not extracted using this buffer [12]. Some procedures are recommended for the extraction of soluble Cr(VI). In such cases a phosphate buffer or water was used for extraction [5,13]. Taking into account the above data, effective and reliable methods for extracting soluble and insoluble Cr(VI) from solid samples without Cr(III) oxidation or Cr(VI) reduction are further required.

In this paper a novel procedure for Cr(VI) extraction from solid samples is evaluated. For a dissolution of soluble and insoluble forms of Cr(VI) an ammonia buffer containing EDTA was proposed. In this extraction procedure the metal ion that form an insoluble chromate was complexed with EDTA, and Cr(VI) as a soluble salt goes into the solution. When the procedure was applied to the extraction of soluble, sparingly soluble and insoluble Cr(VI) a satisfactory recovery was obtained and the reduction of Cr(VI) or oxidation of Cr(III) was not observed.

2. Experimental

2.1. Apparatus

Spectrophotometric measurements were made using Spekol 210, Germany. An extraction was carried out in an ultrasonic bath Sonic 3, Poland. The temperature of extraction was controlled using a thermostat PolyScience, USA. Solid samples were homogenised in a ball mill KM 1, Germany. A centrifuge type 310, Poland, was used.

2.2. Reagents

Ammonium sulphate/ammonium hydroxide buffers were prepared from reagent grade H_2SO_4 and ammonium hydroxide obtained from POCh, Poland. 0.2 mol L^{-1} EDTA was prepared from Na_2EDTA and ammonium hydroxide. Standard solutions of Cr(VI) and Cr(III) at concentration 1 g L^{-1} were obtained from Fluka. Insoluble chromate salts $PbCrO_4$, $BaCrO_4$ were obtained from Fluka. SiO_2 (naturally occurring microcrystalline silica) was obtained from Sigma-Aldrich, USA. Certified reference material (CRM) 013 Paint Chips was obtained from Resource Technology Corporation, USA. A diphenylcarbazide (DPC) solution was prepared by a dissolution of 20 mg of reagent in 10 ml of ethanol, addition of 25 ml of 2 mol L^{-1} H_2SO_4 and then dilution to 50 mL with H_2O.

2.3. Preparation of samples with known concentration of $PbCrO_4$, $BaCrO_4$ or $SrCrO_4$

The mixtures of $PbCrO_4$, $BaCrO_4$ and $SrCrO_4$ containing 0.8% and 400 mg kg^{-1} of Cr(VI) were prepared by serial dilution of $PbCrO_4$, $BaCrO_4$ or $SrCrO_4$ with SiO_2. For example to prepare the mixture containing 0.8% Cr(VI) as $PbCrO_4$, 200 mg $PbCrO_4$ was mixed with 3.822 g SiO_2 and homogenised for 1 h in ball mill. The mixture containing 400 mg kg^{-1} Cr(VI) as $PbCrO_4$ was additionally analysed using extraction with 0.28 mol L^{-1} Na_2CO_3 + 0.5 mol L^{-1} NaOH at temperature of extraction close to 95 °C. The obtained extracts were analysed by a spectrophotometric method based on Cr(VI)–diphenylcarbazide reaction. The result of 10 determinations was 397 mg kg^{-1} with standard deviation 5.4 mg kg^{-1}. The obtained results show that dilutions of $PbCrO_4$ with SiO_2 were done correctly.

2.4. Preparation of paint chips sample

Visual observation shows that paint chips certified reference material CRM013 is not homogeneous, so before the extraction it was homogenised. To avoid the formation of conglomerates in the course of homogenisation of the sample it was mixed with SiO_2. One part of SiO_2 was added to one part of the sample, and such prepared sample was homogenised in the ball mill for 60 min.

2.5. Standard procedure for extraction of Cr(VI) from solid samples

Seventy-five to hundred milligrams of the sample was weighed into a glass vial of volume 22 and 10 mL of the extraction solution containing 0.05 mol L^{-1} $(NH_4)_2SO_4$ + 0.01 mol L^{-1} EDTA + NH_4OH (pH 8.5 or 9.5) was added. Then a small magnetic stirring bar was put to vial and the extraction was carried out in a thermostatised ultrasonic bath for 30 min at 40 °C. The presence of magnetic stirring bar prevents sedimentation of the solid sample. Then the extract with the sample was cooled to room temperature and centrifuged for 5 min.

2.6. Determination of Cr(VI) by spectrophotometry

An aliquot of the extract of the analysed sample was pippeted into a glass bottle. Then an adequate amount of 2 mol L^{-1} H_2SO_4 was added to acidify the sample to pH about 2. Next the solution was diluted to 5 mL with H_2O and 0.3 mL of DPC solution was added. After an equilibration time of 5 min absorbance was measured at 540 nm.

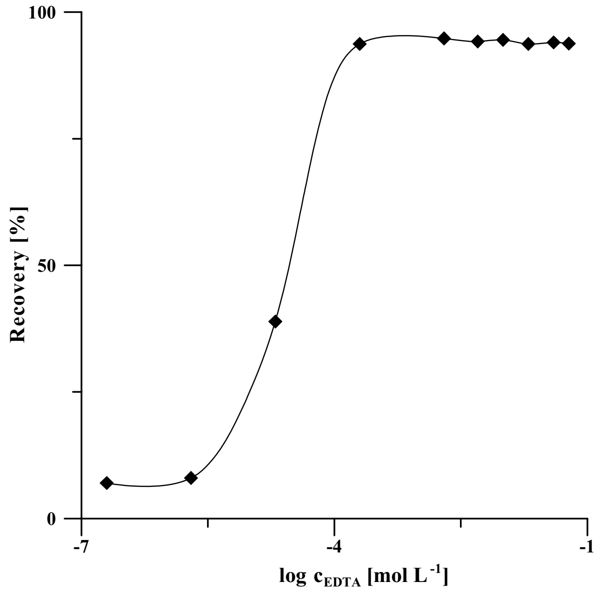

Fig. 1. Effect of EDTA concentration in the ammonia buffer on Cr(VI) recovery from a sample containing 400 mg kg^{-1} Cr(VI) as $PbCrO_4$ in a SiO_2 matrix. Ammonia buffer 0.05 mol L^{-1} $(NH_4)_2SO_4 + NH_4OH$ (pH 8.0).

3. Results and discussion

Preliminary experiments showed that the addition of EDTA to the ammonia buffer used for extraction of soluble and sparingly soluble forms of Cr(VI) [12] can also be used for the extraction of insoluble forms of Cr(VI), so optimisation of the extraction procedure was performed. For study a sample containing 400 mg kg^{-1} of insoluble Cr(VI) as $PbCrO_4$ in SiO_2 matrix was used.

3.1. Effect of EDTA concentration

The extraction of Cr(VI) was performed using standard conditions, but the concentration of EDTA was changed from 0 to 0.06 mol L^{-1}. The results obtained are presented in Fig. 1. The results show that the addition of EDTA to the ammonia buffer drastically influences the extractability of $PbCrO_4$. Although an acceptable recovery of insoluble Cr(VI) was obtained at EDTA concentration of 2×10^{-4} mol L^{-1} for further measurements the concentration of EDTA of 0.01 mol L^{-1} was chosen, as EDTA in real samples can be partially consumed by the formation of complexes with other metal cations present in the sample.

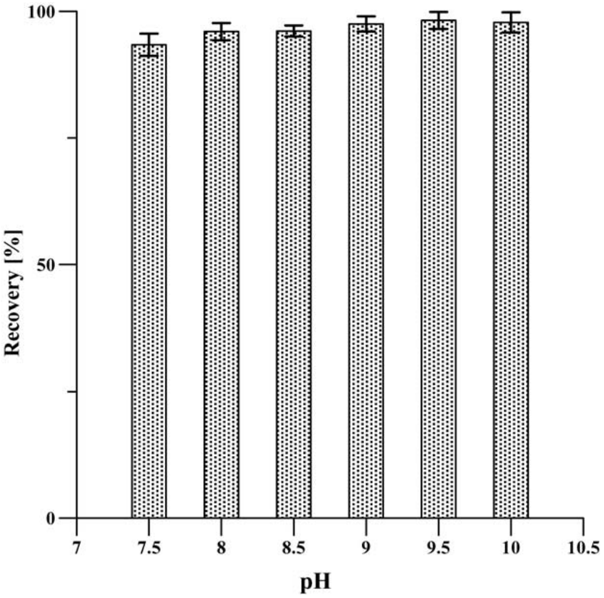

Fig. 2. Effect of the pH of ammonia buffer 0.05 mol L^{-1} $(NH_4)_2SO_4 + NH_4OH + 0.01$ mol L^{-1} EDTA on Cr(VI) recovery from a sample containing 400 mg kg^{-1} Cr(VI) as $PbCrO_4$ in a SiO_2 matrix. Error bars correspond to 1 S.D.

3.2. Effect of pH of extraction

The extraction process was carried out using standard conditions, but pH was changed from 7.5 to 10. The results obtained are presented in Fig. 2. The results show that in the whole range of pH studied good recoveries of Cr(VI) were obtained. To choose optimal extraction pH the following data should be taken into account: at pH higher than 9.5 Cr(III) can be easily oxidised as shown in [14], while when pH decreases the oxidation potential of Cr(VI) increases and Cr(VI) can be reduced to Cr(III). From the results presented in Fig. 2 it is hard to choose the best pH value so for further studies solutions of pH 8.5 and 9.5 were selected.

3.3. Effect of temperature of extraction

The extraction process was carried out using standard conditions, but the temperature of extraction was changed from 25 to 40 °C. The results obtained are presented in Table 1. The results show that for both extraction mixtures of pH 8.5 and 9.5 the recovery of Cr(VI) increases slightly with the increase of the temperature of extraction. For further stud-

Table 1
Effect of temperature on the extraction recovery of Cr(VI) from a sample containing 400 mg kg^{-1} Cr(VI) as $PbCrO_4$ in a SiO_2 matrix

	T [°C]			
	25	30	35	40
Recovery in % for buffer A	91.6 (2.8)	94.6 (1.6)	95.4 (1.5)	96.1 (1.5)
Recovery in % for buffer B	92.5 (2.3)	92.0 (1.2)	93.2 (1.8)	94.9 (1.4)

In brackets the relative standard deviations in % are given (*n* = 5). For extraction buffers containing 0.05 mol L^{-1} $(NH_4)_2SO_4 + NH_4OH + 0.01$ mol L^{-1} EDTA of pH 8.5 (A) and 9.5 (B) were used.

Table 2
Effect of concentration of the ammonia buffer on Cr(VI) recovery from a sample containing 400 mg kg^{-1} Cr(VI) as $PbCrO_4$ in a SiO_2 matrix

Buffer concentration [mol L^{-1}]	Recovery in % for buffer of pH	
	8.5	9.5
0.01	94.1 (1.1)	95.8 (1.7)
0.025	93.5 (1.8)	94.4 (1.4)
0.05	93.8 (1.4)	95.4 (1.8)
0.075	96.1 (1.2)	96.0 (1.2)
0.1	95.8 (1.5)	93.8 (2.0)

In brackets the relative standard deviations in % are given ($n = 5$).

ies the temperature of extraction of 40 °C was chosen since extraction of Cr(VI) was optimised at this temperature.

3.4. Effect of concentration of ammonia buffer

The extraction process was carried out using standard conditions, but the concentration of the ammonia buffer was changed from 0.01 to 0.1 mol L^{-1}. The results obtained are presented in Table 2. The results show that independently of the pH of the extraction mixture, a change of the ammonia buffer concentration does not significantly influence the recovery of Cr(VI). For further studies a 0.05 mol L^{-1} ammonia buffer was chosen for comparability with previously published works [8–12].

3.5. Effect of sample to extraction mixture ratio

The extraction process was carried out using standard conditions, but the mass of the sample was changed from 80 to 1000 mg. The results obtained are presented in Table 3. Independently of the sample to extraction solution ratio an acceptable recovery was obtained. Taking into account the fact that in the course of the extraction of real samples solubilised Cr(VI) can be adsorbed on the solid sample [15], a mass of the sample of about 100 mg is recommended for the extraction using 10 ml of the extraction mixture.

3.6. Effect of extraction time

The extraction process was carried out using standard conditions using buffer of pH 9.5, but the extraction time was changed from 1 to 60 min. For study a synthetic sample containing 400 mg kg^{-1} Cr(VI) as $PbCrO_4$ and paint chips certified reference material was chosen. The results obtained are presented in Fig. 3. The data show that although an extraction time of 1 min is sufficient to obtain an acceptable recovery of Cr(VI) from synthetic sample, an extraction time above 20 min is necessary for the extraction of Cr(VI) from real sample. Such different results are probably connected with the different sizes of the particles in synthetic and real samples, which influences the rate of the extraction process.

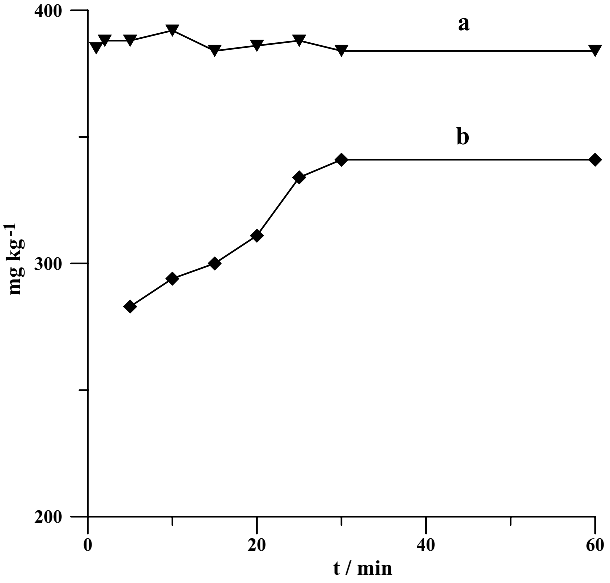

Fig. 3. Influence of the extraction time on the results of Cr(VI) determination in synthetic sample containing 400 mg kg^{-1} Cr(VI) as $PbCrO_4$ in a SiO_2 matrix (a) and paint chips certified reference material CRM013 (b).

3.7. Recovery of insoluble, sparingly soluble and soluble Cr(VI)

The proposed method was optimised for insoluble Cr(VI) added as $PbCrO_4$. According to literature data [12] the ammonia buffer itself extracts quantitatively sparingly soluble and soluble Cr(VI). To confirm that the ammonia buffer containing EDTA can be used also for extraction of other insoluble Cr(VI) compounds as well as sparingly soluble and soluble Cr(VI) compounds additional experiments were performed. The mixture containing 0.05 mol L^{-1} $(NH_4)_2SO_4 + NH_4OH$ + 0.01 mol L^{-1} EDTA of pH 9.5 was applied to the extraction of Cr(VI) from the samples containing 400 mg kg^{-1} of insoluble Cr(VI) added as $BaCrO_4$ and 400 mg kg^{-1} of sparingly soluble Cr(VI) added as $SrCrO_4$. It was found that the recoveries of Cr(VI) were 96.5 and 97.0% with standard deviations of 2.1 and 1.8%, respectively. The

Table 3
Recovery of Cr(VI) in % from a sample containing 400 mg kg^{-1} Cr(VI) as $PbCrO_4$ in a SiO_2 matrix using a different sample to extraction buffer solution ratio

pH of the buffer	Mass of the sample (mg)				
	80	200	300	500	1000
8.5	95.7 (1.7)	96.6 (2.0)	96.0 (1.4)	95.3 (1.7)	96.5 (1.3)
9.5	96.5 (2.1)	98.0 (1.5)	97.0 (1.4)	97.4 (1.2)	98.1 (1.6)

In brackets the relative standard deviations in % are given ($n = 5$). Each extraction was carried out using 10 ml of the solution 0.05 mol L^{-1} $(NH_4)_2SO_4 + NH_4OH$ + 0.01 mol L^{-1} EDTA. Extraction time—30 min; extraction temperature—40 °C.

Table 4
Results of Cr(VI) determination (in mg kg^{-1}) in paint chips certified reference material CRM013 using different methods of extraction

Sample	Method of extraction		
	Proposed method	0.28 mol L^{-1} Na_2CO_3 + 0.5 mol L^{-1} NaOH [3]	10% Na_2CO_3 + 2% $NaHCO_3$ + $MgSO_4$ [6]
CRM013	345 (4.1)	352 (3.4)	359 (4.0)
CRM013 + 2600 mg kg^{-1} Cr(III)	338 (6.2)	826 (5.8)	385 (5.5)

In brackets the relative standard deviations in % are given (n = 5).

recovery of extraction of soluble Cr(VI) added as K_2CrO_4 was 98.4% with standard deviation 1.3%. The above data show that the proposed extraction mixture can be used to extract insoluble, sparingly soluble and soluble Cr(VI).

3.8. *Study of oxidation of Cr(III) to Cr(VI)*

To investigate possible oxidation of Cr(III) to Cr(VI), an extraction was carried out from the sample containing SiO_2 and Cr(III). Cr(III) as $CrCl_3$ was added to the extraction mixture of pH 9.5 to concentration of 0.001 mol L^{-1}. The obtained results show that the concentration of Cr(VI) present in the extract was below the detection limit of the method used. It means that the percentage of oxidation of Cr(III) was below 0.01%. The obtained data are in agreement with the results reported in papers [8,14], where it was stated that the presence of complexing agents such as ammonia or EDTA minimises the speed of the oxidation process of Cr(III) to Cr(VI).

3.9. *Analysis of real sample*

The best way to validate a new procedure of extraction is the application of the procedure to the analysis of certified reference material, although the certified reference material for Cr(VI) does not contain insoluble Cr(VI) [12,16]. Taking into account the above data for study we chose a certified reference material certified only for total chromium. According to literature data [9,11] certified reference material CRM013 paint chips contains Cr(VI). This material was analysed using ammonia buffer of pH 9.5 containing EDTA according to the proposed extraction procedure, and the obtained results were compared with the results obtained using two accepted procedures for Cr(VI) extraction from solid samples described in the literature. The results obtained are presented in Table 4. This table also presents the results of analyses obtained for this material spiked with Cr(III). Practically the same results for Cr(VI) determination in a paint chips sample were obtained using all the procedures of extraction. When the sample was spiked with Cr(III) the result of Cr(VI) determination using extraction with 0.28 mol L^{-1} Na_2CO_3 + 0.5 mol L^{-1} NaOH was higher than the results obtained by two other procedures. Such results are in agreement with literature data [2], where it was reported that extraction with 0.28 mol L^{-1} Na_2CO_3 + 0.5 mol L^{-1} NaOH leads to oxidation of Cr(III) to Cr(VI). Analyses of paint chips sample spiked with Cr(VI) as $PbCrO_4$ were also performed. The recovery of Cr(VI) using the proposed extraction method equal to 94.1% with standard deviation 4.3% was obtained, which indicates that the matrix of the sample does not disturb the recovery but only slightly influences the precision of the measurements. The obtained results show that the method proposed can be used for the extraction of Cr(VI) from solid samples.

Cr(VI) from the paint chips sample was also extracted with H_2O and it was found that the sample contains 252 mg kg^{-1} of soluble Cr(VI). The results obtained for Cr(VI) are higher than 54.4 mg kg^{-1} as reported in the papers [9,11]. Lower results reported in literature can be ascribed to the fact that the material in those studies was probably not homogenised or to the instability of chromium forms in time.

4. Conclusions

A novel procedure for the extraction of soluble, sparingly soluble and insoluble forms of Cr(VI) from solid samples was presented. Due to the addition of EDTA to an ammonia buffer, the efficiency of the extraction of insoluble Cr(VI) as $PbCrO_4$ or $BaCrO_4$ drastically increases and reaches an acceptable value. The presence of complexing agents such as ammonia and EDTA in the extraction mixture also reduces the oxidation Cr(III), which is another advantage of the proposed procedure.

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