

Chromium(III) Determination with 1,5-Diphenylcarbazide Based on the Oxidative Effect of Chlorine Radicals Generated from CCl₄ Sonolysis in Aqueous Solution

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Oxidation of Cr(III) during sonication in carbonated aqueous solutions saturated with CCl₄ leads to the quantitative formation of Cr(VI) and provides a simple and rapid method for spectrophotometric chromium determination with 1,5-diphenylcarbazide. The key to this method is the production of chlorine radicals when aqueous solution saturated with CCl₄ is exposed to ultrasonic waves of 40 kHz. The effects of sonication period, CCl₄ solution volume, acidity, and interferences were discussed. The time required for a single determination is lower than 2 min. The relative standard deviation obtained for aqueous solutions with 1 µg of Cr was <2% (*N* = 10) and the calculated detection limit (3σ) was 5 ng of Cr.

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Introduction

The low sensitivity of the spectrophotometric methods related to trivalent chromium and the slow reactions performed between the chromogenic reagent and the strongly hydrated Cr(III) ions lead to the application of selective methods for Cr(VI). In this sense, Cr(III) is commonly determined by the reaction with 1,5-diphenylcarbazide (DPC), after the oxidation to Cr(VI). The ordinary methods employed to oxidize Cr(III) make use of H₂O₂ in alkaline media,¹ persulfate with Ag⁺ and permanganate.² The principle of this method is based on the selective reaction of Cr(VI) with DPC in acid media, permitting the determination at the µg l⁻¹ level.³

Sonochemical formation of oxidizing species such as hydrogen peroxide, nitric and nitrous acids was observed⁴⁻⁶ and this event has already been applied for spectrophotometric Ni²⁺ determination with dimethylglyoxime.⁷ Oxidative species can be yielded by the collapse of cavitation bubbles that occur when aqueous solutions are subjected to ultrasonic waves. During a rarefaction sonic cycle, gases and vapors present in the medium are diffused to the cavities and the cavitation bubble collapses at the compression cycle. The energy produced by the cavitation collapse can lead to the cleavage of chemical bonds, yielding free radicals that can be combined to generate new species in the sonicated medium.⁵

The degradation of CCl₄ and many organic solvents by ultrasonic irradiation, allied or not with other types of energy, such as electromagnetic and thermal, was studied in order to

remove organic pollutants from waste water.⁸⁻¹³ The production of oxidizing species by sonochemical degradation of CCl₄ in aqueous solution was reported in 1950.¹⁴ In ultrasonic degradation of CCl₄, different intermediaries (Cl₂, HClO, C₂Cl₄ and C₂Cl₆) and final products (HCl, CO and CO₂) were detected.¹⁵⁻¹⁷ Therefore, during sonication of the CCl₄ aqueous solution, organic chlorinated species were consecutively produced and degraded, resulting in a pH decrease and in increasing chloride and CO₂ concentrations.¹⁵

In this work the potentiality of the oxidizing species produced during CCl₄ ultrasonic degradation to oxidize Cr(III) in aqueous solution was evaluated. The effects of sonication time, CCl₄ saturated aqueous solution amount, acidity and the influence of different ions for Cr(III) oxidation were investigated. The proposed method for Cr(III) determination was evaluated using a recovery test in water samples.

Experimental

Instruments

A commercial ultrasonic cleaner bath (VWR Instruments Aquasonic Model 75D) was employed to irradiate sample solutions at 40 kHz. A spectrophotometer (Femto 432) equipped with a glass cuvette (10-mm optical path) was used for chromium determination. All pH measurements were performed using a pH meter (Hanna Checker 1) equipped with a glass electrode.

The profile of chloride generation during ultrasonic irradiation was potentiometrically monitored with a Micronal B374 potentiometer, making use of a continuous flow system equipped with a tubular ion selective electrode with crystalline

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membrane for chloride^{18,19} and AgCl/Ag as reference electrode. For this evaluation, the sample propulsion at 3.5 ml min⁻¹ was performed with a peristaltic pump (Gilson Minipuls 3).

Reagents and solutions

All chemicals used were of analytical grade and the solutions were prepared using deionized water. HNO₃ solutions were made from concentrated HNO₃. The 1000 mg l⁻¹ of Cr₂O₇²⁻ and Cr(III) stock solutions were prepared using K₂Cr₂O₇ and CrCl₃ (Titrisol, Merck, Germany). Standard solutions from 0.1 to 6 mg l⁻¹ Cr(III) were prepared by the proper dilution of stock solutions. The Cr complexing reagent solution was prepared by dissolving 0.05 g of 1,5-diphenylcarbazide in 2 ml of acetic acid and diluting this to 25 ml with water. NaHCO₃ was used to prepare a 0.01 mol l⁻¹ solution.

Fe²⁺ solutions were prepared from Fe(NH₄)₂(SO₄)₂·6H₂O. The 1 g l⁻¹ 1,10-phenanthroline solution was prepared in water. Deionized water saturated with CCl₄ was obtained by adding 2 drops of this reagent in 400 ml of water before stirring the mixture for 2 h at 25 ± 1 °C and separating the aqueous phase before the experiments.

Procedures

All glassware and bottles used were cleaned in 1.8 mol l⁻¹ HNO₃ for 12 h and rinsed with deionized water before use. All experiments assisted by ultrasonic waves were conducted in the central zone of the ultrasonic bath, where the effects of ultrasonic irradiation for the equipment employed are intensified.²⁰

Chloride ion generation was monitored by irradiating 6 ml of CCl₄ saturated aqueous solution from 0 to 40 s, continuously pumping this solution through the tubular chloride electrode in recycle mode at 3.5 ml min⁻¹. The hydrogen ion production by ultrasonic irradiation was monitored in batch using the same volume of CCl₄ solution from 0 to 40 s to compare with Cl⁻ generation; pH variation was also evaluated for up to 15 min of carbon tetrachloride solution ultrasonic irradiation.

The evaluation of oxidizing species produced by sonochemical degradation of CCl₄ was carried out by determining the residual Fe(II) after sonication of CCl₄ aqueous solution with 1,10-phenanthroline. Thus, 4 ml of CCl₄ saturated aqueous solution, with or without Fe(II), was sonicated up to 50 s, mixed with chromogenic reagent. The signal obtained was measured at 508 nm. For the systems sonicated without Fe(II), 1 ml of 40 mg l⁻¹ Fe(II) was immediately added after sonication.

In order to evaluate chromium oxidation, 1 ml of Cr(III) solution and 500 µl of 0.01 mol l⁻¹ NaHCO₃ were added into a 5 ml volumetric flask and the volume was taken to mark with the CCl₄-saturated aqueous solution. This solution was transferred to a 10 ml borosilicate beaker (i.d. = 22 mm, e.d. = 24.5 mm, h = 36 mm) for sonication. Irradiation periods from 0.2 to 10 min were evaluated and the temperature was maintained at 25 ± 1 °C. During sonication, the water in the ultrasonic bath was continuously changed at 500 ml min⁻¹. After irradiation, 200 µl of 1 mol l⁻¹ H₂SO₄ and 500 µl of DPC solution were added into the beaker. Analytical signals were measured at 540 nm.

Waste and tap water samples were used to carry out recovery tests for the Cr(III) determination. These studies were performed by adding 1 ml of 0.50 or 1.00 mg l⁻¹ Cr(III) solution, 500 µl of 0.01 mol l⁻¹ NaHCO₃ and 3 ml of the sample saturated with CCl₄. Waste and tap water samples were irradiated for 10 and 3 min, respectively. Following sonication, the same procedure was repeated.

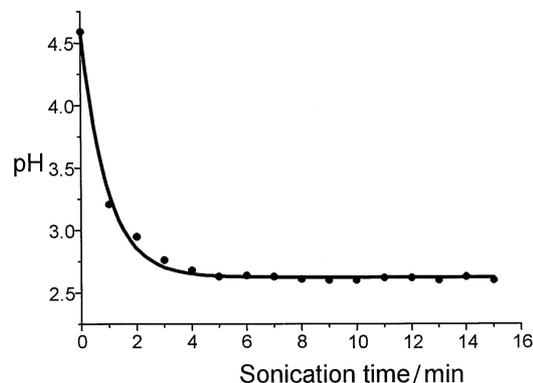


Fig. 1 pH variation for 5.0 ml CCl₄-saturated aqueous solution with sonication time.

Results and Discussion

Sonolysis of CCl₄

When a saturated aqueous solution of CCl₄ is sonicated, some molecules of the chlorinated compound are encouraged to diffuse and decompose inside cavitation bubbles, since the vapor pressure of CCl₄ is higher than water. The first step of CCl₄ degradation is the cleavage of the carbon-chlorine bond, generating trichloromethyl and chlorine radicals according to Eq. (1).



The chlorine radical formed can react with water molecules, yielding hydrogen chloride, reaction (2). However, other possibilities that involve the same product formation can be proposed, Eqs. (3) to (5):



The pH values of the CCl₄ solution after sonication were evaluated and the pH variation for different sonication periods can be seen in Fig. 1. By increasing the irradiation time up to 5 min the solution pH was decreased. The pH decrease depends on the volume of irradiated solution, CCl₄ concentration and properties of the sonicator (frequency, power and wave amplitude). By handling the same data set, one can deduce that, during the sonication for the first 3 min of 5 ml CCl₄-saturated aqueous solution under the specified conditions, the hydrogen ion quantity had linearly increased ($R = 0.9994$) at a rate of 47 ± 2 nmol s⁻¹.

The monitoring of chloride ion generation confirmed the interaction between chlorine radicals and water molecules leading to HCl production. Figure 2 shows the profile of hydrogen and chlorine ion production up to 40 s of sonication. For sonication time higher than 10 s, the Cl⁻ generated was higher than H⁺ because there was the possibility of interaction between two chlorine radicals to produce Cl₂ which could be decomposed into the bulk solution, generating chloride ions. Notwithstanding, the production of H⁺ ions depended on the

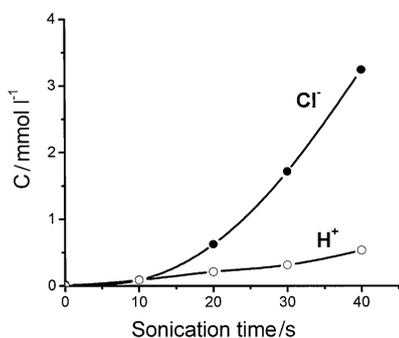


Fig. 2 Comparison of hydrogen and chloride ion generation by sonication of CCl_4 .

presence of one chlorine radical in gas-liquid interface of the collapsed bubble that would react with one water molecule, Eq. (2). However, as the free radicals are unstable, they lead to random reactions with any neighboring species, such as N_2 , O_2 , $\cdot\text{Cl}$, $\cdot\text{OH}$ and $:\text{CCl}_2$.

The production of oxidizing species after sonication of the CCl_4 solution was evaluated. Reactions (4) and (5) indicate mechanisms for HClO formation, but other molecular species (Cl_2 and H_2O_2) can be produced, as proposed in reactions (6) and (7).



In order to evaluate the reactivity of the oxidizing species sonochemically generated, water saturated with CCl_4 was sonicated at different interval times and the solutions formed were used to oxidize Fe(II) to Fe(III) . The production of oxidizing species was photometrically monitored at 508 nm by carrying out Fe(II) disappearance using the 1,10-phenanthroline method. The oxidation of Fe(II) was selected to evaluate the oxidizing species produced by sonication, since the conversion of Fe(II) to Fe(III) in aqueous solution by ultrasonic wave action was the system used in the pioneer investigations related to OH radical production.²¹ As can be seen in Fig. 3, Fe(II) added after CCl_4 aqueous solution sonication was completely oxidized after 40 s. The oxidation reaction involved in Fe(II) oxidation can be related with Cl_2 or HOCl produced by the sonochemical process. Since both reactions involve the transfer of two electrons, Fe(III) formation rate was calculated at 28 nmol s^{-1} and the production rate of oxidizer species was 14 nmol s^{-1} .

The generation of chemical species induced by ultrasonic waves is a competitive process, since the chlorine radical can react with water producing HCl , Eq. (2), or alternatively the same free radical can produce Cl_2 or HClO , Eqs. (4) to (6). As the production rate for HCl was higher than that calculated for Cl_2 , it can be assumed that $\text{Cl}\cdot$ reacts in higher proportion with water molecules present on the interface of cavitation bubbles.

The efficiency of sonochemical oxidation of Fe^{2+} in water and CCl_4 aqueous solution was compared. The process of Fe^{2+} -1,10-phenanthroline fading in both cases is shown in Fig. 4. In this condition the calculated Fe^{2+} oxidation rates in water and CCl_4 solution were 1.3 and 24 nmol s^{-1} , respectively. These results can be explained based on the higher vapor pressure of CCl_4 compared with that of H_2O ,¹⁵ and the bond energies of C-Cl and O-H, 73 and $119 \text{ kcal mol}^{-1}$, respectively,¹⁷ leading to a higher diffusion of CCl_4 to the cavitation bubble and Cl

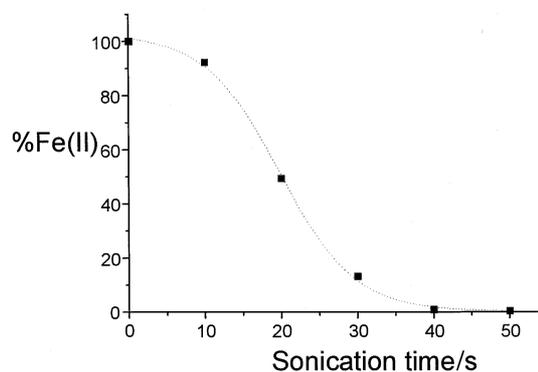


Fig. 3 Oxidation of Fe(II) by prior sonication of 4 ml CCl_4 saturated aqueous solution.

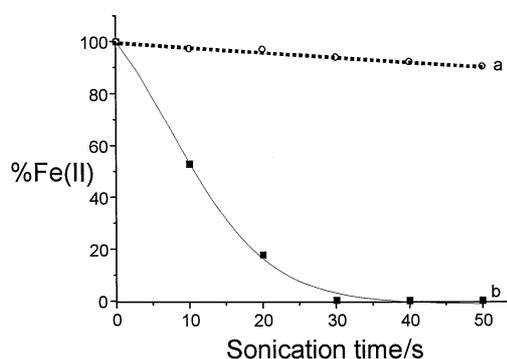


Fig. 4 Comparison of Fe(II) oxidation by irradiating in (a) water and (b) CCl_4 aqueous solution.

radical production in the sonicated medium.

The production of chlorine radical was also observed by irradiating aqueous solutions of CHCl_3 , CH_2Cl_2 and $\text{C}_2\text{H}_3\text{Cl}_3$. The formation rates of chlorine radical for these chlorinated compounds were lower than those for CCl_4 , due to their properties (solubility, vapor pressure and molecular weight).

Sonochemical oxidation of Cr(III)

As previously mentioned, Cr(III) oxidation is ordinarily performed by adding a powerful oxidizing agent. Chromium oxidation is most easily performed in alkaline media, since in this condition the standard potential is diminished. As discussed above, the solution produced by CCl_4 aqueous solution sonication had increased the concentrations of oxidizing agent and H^+ . However, the oxidation of Cr(III) was only carried out by sonicating CCl_4 aqueous solutions in the presence of metal ions. Although Cr(III) oxidation has been observed by sonicating in water and CCl_4 aqueous solution, for analytical purposes, the latter was most advantageous, since analytical throughput is increased. The advantage of using the CCl_4 aqueous solution can be illustrated by comparing the data obtained when a solution containing $1 \mu\text{g}$ of Cr was sonicated with water and CCl_4 solution when compared with $\text{Cr-Cr}_2\text{O}_7^{2-}$ solution in the same concentration. While in the first case only 30% of Cr(III) was oxidized by sonicating water over 15 min, for CCl_4 solution *ca.* 70% of the metal ion was oxidized in 60 s.

Effect of sonication time

As previously discussed, the oxidation of Cr(III) depends on the parameters of the ultrasonic wave generator. Since a

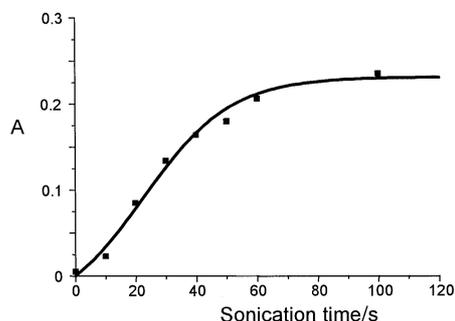


Fig. 5 Effect of sonication time on Cr(III) oxidation in CCl_4 -saturated aqueous solution.

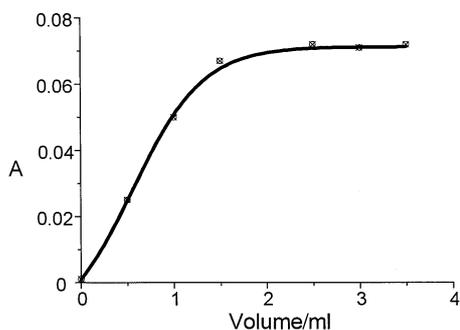


Fig. 6 Effect of CCl_4 saturated aqueous solution volume on Cr(III) oxidation by CCl_4 -saturated aqueous solution sonicated over 60 s.

commercial sonicator was employed, only the sonication period and temperature could be varied to maximize the conversion. In this sense, as the chlorine radicals formed during CCl_4 decomposition increase with sonication time, the Cr(III) oxidation rate was evaluated by varying the irradiation time (Fig. 5). For this evaluation, 5 ml of solution saturated with CCl_4 containing $10 \mu\text{g}$ of Cr(III) was sonicated under the above mentioned conditions. The results indicated that the conversion increased with sonication time, reaching the maximum at 60 s of irradiation. This sonication time was then maintained for the following experiments.

Effect of CCl_4 solution volume

The quantity of chlorine radicals released into the bulk solution was directly related to the amount of CCl_4 that can diffuse to the transient cavities. Thus, for $1 \mu\text{g}$ of Cr(III) and maintaining the final volume at 5 ml, the maximum conversion was obtained when the volume of CCl_4 saturated aqueous solution was maintained higher than 2 ml (Fig. 6). Therefore, the addition of 3 ml of CCl_4 saturated aqueous solution used for successive optimization method tests was selected.

Effect of acidity

The trivalent chromium ion is stable in acid media, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, while ultrasonic oxidation must be carried out in neutral or alkaline medium. Since the CCl_4 degradation led to a pH decrease, Cr(III) was not oxidized by running the ultrasonic irradiation without the addition of alkaline or neutral buffer solution. The variation of Cr(III) oxidation with pH in solutions with and without carbonate buffer solution is depicted in Fig. 7. In fact, in the presence of HCO_3^- the analytical signal for a pH range between 6 and 8 was 3 times higher than those obtained in the absence of carbonate without significant variation (6%). For

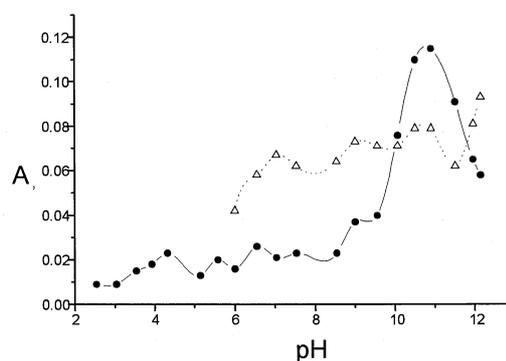


Fig. 7 Variation of Cr-DPC absorbance with pH. (Δ) CCl_4 -saturated aqueous solution sonicated over 1 min buffered with $0.01 \text{ mol l}^{-1} \text{HCO}_3^-$ and (\bullet) without buffer.

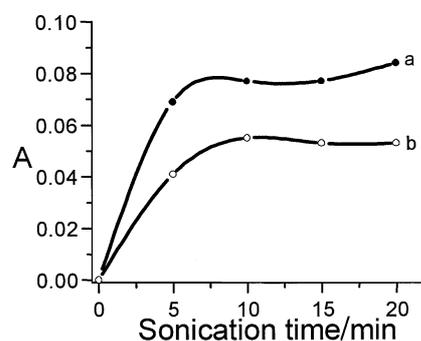


Fig. 8 Effect of Co^{2+} on recovery test of Cr(III) in waste water (a) by adding Co(II) and, (b) without Co(II).

the curve related to the sonication of Cr(III) solution saturated with CCl_4 without added HCO_3^- , the chromium oxidation only occurred in alkaline medium ($\text{pH} > 9$) because the solution pH decreased to 3 during CCl_4 degradation, creating a drawback for Cr(III) oxidation.

The maximum Cr(III) oxidation occurs at a pH from 6.7 to 7.3. By use of a bicarbonate concentration higher than 0.01 mol l^{-1} , an increased CO_2 formation during sonication was observed that led to a quenching of the cavitation process.^{22,23}

Interferences

The species capable of being oxidized by chlorine radicals and those that can be associated with these radicals can lead to a decrease in the oxidation rate of Cr(III) during sonication. As the oxidizing agent was generated *in situ*, the $\cdot\text{Cl}$ radical might react with some concurrent species. In this way, it would be essential to enrich the sample solution with CCl_4 to perform the ultrasonic irradiation, in order to warrant the release of sufficient quantities of chlorine radicals to react also with chromium.

The tolerance limits to some species were evaluated and the results are shown in Table 1. These results lead to the conclusion that those species easily oxidized when present in large proportions related to Cr(III), such as Fe(II), sulfite, ammonium, organic compounds, and others, can compete with Cr to Cl radicals in diminishing or extinguishing the Cr(III) oxidation.

Cobalt ion effect

The presence of Co^{2+} in the irradiated system caused a

Table 1 Tolerance limits to some species on Cr(III) oxidation

Ion	Ion/Cr(III)
Fe(II)	<0.05
Pb(II), NO ₂ ⁻	<0.5
Ni(II)	<10
SO ₃ ²⁻	<50

Tolerance of 5% on variation of the signal related to oxidation in the absence of species.

remarkable effect, since only this metallic ion had promoted an increase in Cr(III) oxidation rate, as can be seen in Fig. 8. This effect was most likely related to Co(III) generation during sonication, which caused an improvement in Cr(III) oxidation, since the cobalt ions do not react with DPC.

The reaction between Cr(V) and DPC was earlier studied²⁴ and the results had indicated that the signal related with the reaction of Cr(V) with DPC was 40% lower than that for Cr(VI) with the same reagent. When the ultrasonic oxidation of Cr(III) was carried out in the absence of Co(II), the signals were between 60 and 75% of that obtained by employing the same amount of chromium, as Cr(VI). This suggested that Cr(V) was generated in the absence of Co(II), while in the presence of this ion, Cr(VI) was produced, since the signals reached up to 100% when compared with the Cr(VI) solutions in the same Cr concentrations. Therefore, Co(II) can be considered as a reaction mediator since it allowed a quantitative conversion to chromate.

Validation test

Ultrasonic oxidation could be employed to a solution containing between 0.1 and 3 µg Cr(III) ($A = 0.0549m + 0.0080$, $R = 0.9993$) in the absence of Co(II) under the studied conditions with a calculated detection limit (3σ) of 5 ng of Cr(III) and a relative standard deviation <2% for 10 determinations. In the presence of cobalt ions as mediator sonochemical oxidation could be employed in a solution containing from 0.05 to 2 µg Cr(III) ($A = 0.0734m + 0.0080$, $R = 0.9991$) with a calculated detection limit (3σ) of 3 ng of Cr and relative standard deviation <2% for 10 determinations.

The validation of the procedure was made through the recovery test for water samples, evaluating the positive effect of the presence of Co(II). Figure 8 shows signal *versus* sonication time curves in the presence and absence of Co(II) in the waste water sample. Following 10 min of ultrasonic irradiation of this sample with or without the addition of Co(II), the Cr(III) conversion to oxidized species was constant. However, in the presence of Co(II), the signal related with the reaction between oxidized chromium and DPC was higher.

Table 2 shows the results for the recovery test of Cr(III) in waste and tap water by adding 0.5 and 1.0 µg of Cr(III). The best recovery data were obtained by adding Co(II) into the sample solution.

Conclusions

The production of reagents *in situ* assisted by ultrasonic irradiation effect was exploited for chromium determination in water samples. The sonolytic CCl₄ degradation led to chlorine radical generation that caused the oxidation of stable ions, such as Cr(III), when present during sonication. Nevertheless, this procedure applied for Cr(III) determination in water samples

Table 2 Recovery test of Cr(III) in water samples

Water sample	Cr(III) added/µg	Cr(III) recovery/µg	%
Waste with Co ²⁺	0.50	0.47 ± 0.01	94 ± 2
	1.00	0.99 ± 0.02	99 ± 2
Waste-free Co ²⁺	0.50	0.47 ± 0.02	94 ± 4
	1.00	0.69 ± 0.03	69 ± 3
Tap with Co ²⁺	0.50	0.48 ± 0.01	96 ± 2
	1.00	0.99 ± 0.01	99 ± 1
Tap-free Co ²⁺	0.50	0.50 ± 0.01	100 ± 2
	1.00	0.87 ± 0.01	87 ± 1

avoids sample manipulations, since the chlorine radicals could degrade inorganic and organic contaminants.

Besides the environmental and health problems associated with CCl₄ use, one advantage related to degradation is the low consumption of reagent, since 2000 l of CCl₄ saturated aqueous solution is prepared with just 1 l of CCl₄. This volume of CCl₄ aqueous solution is enough to carry out more than 500000 determinations of Cr(III) in mineral and tap water samples. It should be mentioned that the excess CCl₄ can be degraded by sonicating the solution over an extended period of time (*ca.* 10 min). Therefore, by employing the same apparatus to discard treatment, the excess CCl₄ will be completely mineralized to produce CO₂ and HCl.

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References

1. J. E. T. Andersen, *Anal. Chim. Acta*, **1998**, 361, 125.
2. Z. Marczenko, "Spectrophotometric Determination of Elements", **1976**, John Wiley, New York.
3. K. Wróbel, K. Wróbel, and P. L. López-de-Alba, *Talanta*, **1997**, 44, 2129.
4. R. S. Souza, M. Korn, L. R. F. Carvalho, M. G. A. Korn, and M. F. M. Tavares, *Ultrasonics*, **1997**, 36, 595.
5. L. R. F. Carvalho, R. S. Souza, B. S. Martins, and M. Korn, *Anal. Chim. Acta*, **1995**, 317, 171.
6. C. A. Wakeford, R. Blackburn, and P. D. Lickiss, *Ultrason. Sonochem.*, **1999**, 6, 141.
7. C. S. Sousa and M. Korn, *Anal. Chim. Acta*, **2001**, 444, 309.
8. A. Bhatnagar and H. M. Cheung, *Environ. Sci. Technol.*, **1994**, 28, 1481.
9. H. M. Cheung, A. Bhatnagar, and G. Jansen, *Environ. Sci. Technol.*, **1991**, 25, 1510.
10. G. E. Orzechowska, E. I. Poziomek, V. F. Hodge, and W. H. Engelmann, *Environ. Sci. Technol.*, **1995**, 29, 1373.
11. H. M. Hung and M. R. Hoffmann, *Environ. Sci. Technol.*, **1998**, 32, 3011.
12. C. Petrier, M. Micolle, G. Merlin, J. L. Luche, and G. Reverdy, *Environ. Sci. Technol.*, **1992**, 26, 1639.

13. E. Naffrechoux, S. Chanoux, C. Petrier, and J. Suptil, *Ultrason. Sonochem.*, **2000**, 7, 255.
 14. A. Weissler, H. W. Cooper, and S. Snyder, *J. Am. Chem. Soc.*, **1950**, 72, 1769.
 15. A. Francony and C. Petrier, *Ultrason. Sonochem.*, **1996**, 3, 77.
 16. A. Alippi, F. Cataldo, and A. Galbato, *Ultrasonics*, **1992**, 30, 148.
 17. I. Hua and M. R. Hoffmann, *Environ. Sci. Technol.*, **1996**, 30, 864.
 18. I. M. P. L. V. O. Ferreira, J. L. F. C. Lima, and L. S. M. Rocha, *Fresenius J. Anal. Chem.*, **1993**, 347, 314.
 19. J. L. F. C. Lima and L. S. M. Rocha, *Int. J. Environ. Anal. Chem.*, **1990**, 38, 127.
 20. C. C. Nascentes, M. Korn, C. S. Sousa, and M. A. Z. Arruda, *J. Braz. Chem. Soc.*, **2001**, 12, 57.
 21. N. Miller, *Trans. Faraday Soc.*, **1950**, 46, 1086.
 22. A. Weissler, *J. Am. Chem. Soc.*, **1950**, 171, 1007.
 23. I. E. ÉI'Piner, "Ultrasound: Physical, Chemical, and Biological Effects", **1964**, Consultants Bureau, New York, 56.
 24. J. M. Eckert, R. J. Judd, P. A. Lay, and A. D. Symons, *Anal. Chim. Acta*, **1991**, 255, 31.
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