

Analytical note

Use of cetyltrimethylammonium bromide as surfactant for the determination of copper and chromium in gasoline emulsions by electrothermal atomic absorption spectrometry [☆]

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Abstract

In this work, the use of cetyltrimethylammonium bromide as surfactant for the preparation of oil-in-water emulsions for the determination of Cu and Cr in gasoline by electrothermal atomic absorption spectrometry (ET AAS) was evaluated. The surfactant amount was tested in the range of 25 to 300 mg, added to 2 ml of gasoline, and completed to 10 mL with 0.1% (v/v) nitric acid solution. 150 mg of surfactant was found optimum, and a sonication time of 10 min sufficient to form an oil-in-water emulsion that was stable for several hours. The ET AAS temperature program was established based on pyrolysis and atomization curves. The pyrolysis temperatures were set at 700 and 1300 °C for Cu and Cr, respectively and the selected atomization temperatures were 2400 and 2500 °C. The time and temperature of the drying stage and the atomization time were experimentally tested to provide optimum conditions. The limits of detection were found to be 5 µg L⁻¹ and 1.5 µg L⁻¹ for Cu and Cr, respectively in the original gasoline samples. The relative standard deviation (RSD) ranged from 4 to 9% in oil-in-water emulsions spiked with 5 µg L⁻¹ and 15 µg L⁻¹ of each metal, respectively. Recoveries varied from 90 to 98%. The accuracy of the proposed method was tested by an alternate procedure using complete evaporation of the gasoline sample. The method was adequate for the determination of Cu and Cr in gasoline samples collected from different gas stations in Salvador, BA, Brazil.

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1. Introduction

The presence of metallic species in fuels can cause problems, such as degradation of the fuel, formation of precipitates, possible damage of motor parts, in addition to the emission of metal compounds to the atmosphere [1,2]. Therefore, except in the form of additives intended to promote specific characteristics, the presence of metals in fuels is usually undesirable even

at low concentration, and their quantification is indispensable to evaluate the quality of fuels and to control potential environmental pollution [3–7].

The quantification of Cu and Cr in gasoline and similar products is the topic of several publications, using different sample preparation procedures and quantification techniques [3,4,8–13]. The cationic surfactant cetyltrimethylammonium bromide (CTAB) has been widely used in several fields for a variety of applications, such as extraction procedures [14], kinetic studies [15], biotechnological and biomedical applications [16], complex reactions [17,18] and improvement of the analytical sensitivity in spectrophotometric determinations [18–21].

Electrothermal atomic absorption spectrometry (ET AAS) has been widely used for the determination of trace levels of metals in different matrices, including fuels and other petroleum

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derivates. However, the low viscosity and surface tension of fuels may impair sample introduction and make the efficient use of an autosampler difficult [4,5,22]. Emulsification is one of the procedures employed to reduce the problems resulting from the direct introduction of petroleum derivates for the determination of metals by atomic spectrometric techniques. The non-ionic surfactant Triton X-100 is generally used for this purpose [3,5,23–25], however, a relatively large quantity of this surfactant, typically between 4 and 20% m/v is necessary to form an emulsion [24,25], and the emulsions are often not stable over longer periods of time.

In this work the use of CTAB and sodium dodecylhydrogensulfate (SDS) have been evaluated as surfactants for gasoline sample preparation for the determination of Cr and Cu at $\mu\text{g L}^{-1}$ levels using ET AAS. The aim of this study was to investigate whether stable oil-in-water emulsions can be prepared with a smaller quantity of surfactant and a higher amount of sample compared to Triton X-100, which would also imply a lower dilution factor, i.e. better limits of detection. Samples were prepared by mixing the gasoline samples with 0.1% (v/v) nitric acid solution and with the surfactant, using the effect of ultrasound irradiation. The procedure was applied to analyze different samples of commercial gasoline sold in the city of Salvador, BA, Brazil.

2. Experimental

2.1. Instrumentation

A Varian SpectrAA 220Z atomic absorption spectrophotometer with Zeeman-effect background correction (Mulgrave, Victoria, Australia), equipped with a model GTA 110 graphite tube atomizer, a PSD auto-sampler and Varian hollow cathode lamps was used for all measurements. The conditions were set according to the manufacturer's instructions. Pyrolytic graphite-coated graphite tubes with a center-fixed platform (Varian, part number: 63-100026-00) were used. Argon 99.996% (White Martins, São Paulo, Brazil) was employed as a purge and protective gas. An injection volume of 15 μL was used for all experiments and three replicates were measured unless otherwise stated. All measurements were based on integrated absorbance.

A VWR Signature model 75D ultrasound bath (Parkway West Chester, PA, USA) was used to irradiate the solutions.

2.2. Reagents and samples

All reagents were at least of analytical grade, and freshly distilled and deionized water (electrical resistivity of 18.0 $\text{M}\Omega\text{ cm}$) was used for dilutions. The nitric acid solution (0.1% v/v) was prepared by diluting concentrated nitric acid (suprapure, Merck, Darmstadt, Germany).

A multi-element aqueous standard with a content of 1000 mg L^{-1} Cr, Cu, Fe, Mn and Ni, sodium dodecylhydrogensulfate (SDS, Merck, Darmstadt, Germany), Cetyltrimethylammonium bromide (CTAB, Aldrich, St. Louis, MO, USA), Triton X-100 (Vetec, Rio de Janeiro, Brazil) and hydrochloric acid (J.T.Baker, Mexico City, Mexico) were used as supplied.

The metal–organic standard containing 10 $\mu\text{g g}^{-1}$ of Cr and Cu was supplied by AccuStandard Inc. (New Haven, USA). Propan-1-ol (Merck, Darmstadt, Germany) was used for the preparation of the metal–organic standard solution.

Gasoline samples were collected from different gas stations in the city of Salvador, BA, Brazil. Samples were filled into 100-mL amber glass bottles and stored at 4 °C to maintain sample integrity, until analysis. The bottles were capped and screwed immediately after introduction of the samples. It should be noted that the ethanol content in Brazilian gasoline is typically between 20 and 25% (v/v).

2.3. Surfactant analysis

The concentration of Cr, Cu, Fe, Mn and Ni in the surfactants Triton X-100, SDS and CTAB was determined by ET AAS using the analyte addition technique based on aqueous standards solutions with the purpose of evaluating the degree of contamination. 100 mg of surfactant was transferred to 10-mL volumetric flasks, dissolved and filled to the mark with 0.1% HNO_3 solution. The heating program used in this procedure was that recommended by the instrument manufacturer.

2.4. Sample preparation

For sample preparation 150 mg of surfactant was placed in a 10-mL volumetric flask and 2 mL of gasoline was added. The system was vigorously agitated and diluted to volume with 0.1% (v/v) HNO_3 solution, as previously described by dos Santos et al. [5]. Then the system was sonicated for 10 min and an emulsion of the oil-in-water (O/W) type was formed. The flasks were closed during ultrasound irradiation. The blank solution was obtained following the same procedure applied for the emulsion preparation but using only the surfactant and 0.1% (v/v) HNO_3 solution, as previously described by Saint'Pierre et al. [3].

2.5. Comparative procedure

Since no certified reference material is available for trace elements in gasoline, the accuracy was checked by comparison with an independent analytical procedure. A sample aliquot of 2 mL was transferred to an Erlenmeyer flask and gently evaporated to near-dryness on a hot plate. The residue was quantitatively transferred into a 10-mL volumetric flask with 2 mL of HCl and filled up with deionized water. The analytes were determined by ET AAS using aqueous calibration standards.

3. Results and discussion

3.1. Surfactant studies

The feasibility of employing SDS or CTAB as surfactants for the gasoline emulsion preparation was evaluated. The main criterion used to choose the surfactant was its solubility in the two immiscible phases, which should be relatively high [23]. For these studies, a qualitative solubility test [5] was carried out: 25 mg of the surfactant was added to 1 mL of nitric acid solution

Table 1
Concentration of various metals in the investigated surfactants

Surfactant	Concentration ($\mu\text{g kg}^{-1}$) ^a				
	Cr	Cu	Fe	Mn	Ni
Triton X-100	0.62±0.03	1.1±0.1	10.2±0.2	5.3±0.3	14.2±0.2
SDS	1.9±0.1	4.3±0.3	13.9±0.9	2.7±0.1	3.4±0.1
CTAB	0.80±0.01	0.86±0.02	17.7±0.5	2.0±0.2	2.5±0.2

^a Mean±S.D.; *n*=3.

and to 1 mL of gasoline, respectively, followed by 30 s of sonication. The homogeneity of the system was then observed. The need for sonication times longer than 1 min to completely dissolve the surfactant or the formation of a heterogeneous system was used as criterion for unsatisfactory miscibility of the surfactant with that volume of solvent. Both surfactants showed good solubility in the aqueous and organic phase.

The second criterion used to evaluate the surfactants was their degree of purity in terms of trace metals. The concentrations of Cr, Cu, Fe, Mn and Ni in SDS, CTAB and in Triton X-100 were determined by ET AAS using the analyte addition technique with aqueous standard solutions.

The concentrations of Fe, Mn and Ni were relatively high in all three surfactants, considering the usually low concentration of these analytes in gasoline samples as is shown in Table 1. Thus, it was concluded that none of the studied surfactants was suitable to be used in the determination of these elements. The concentrations of Cu and Cr were also relatively high in SDS, so that this surfactant was considered unsuitable for the quantification of the specified metals. The concentrations of Cu and Cr in the CTAB and Triton X-100, in contrast, were satisfactorily low. Thus, CTAB was chosen to prepare the gasoline samples.

Several experiments were conducted to determine the minimum quantity of surfactant required to form a stable emulsion. The stability should be sufficient to perform the measurements and to establish the analytical curve. CTAB was tested in the range of 25–300 mg with the gasoline volume fixed at 2 mL. The results indicated that the use of 150 mg of CTAB produced emulsions that remained homogeneous for several hours. The use of CTAB reduces the amount of surfactant required to prepare oil-in-water emulsions of gasoline from typically 4–20% (m/v) in the case of Triton X-100 [16,17] to only 1.5% (m/v).

In previous work [5] it has been found that emulsions sonicated for time periods longer than 4 min resulted in homogeneous systems that remained stable for more than 48 h. Thus, in the present procedure a 10 min sonication time was applied to ensure optimal homogeneity of the system. The emulsions generally showed no phase separation for several days, and in the few cases when separation did occur, the homogeneity could be reestablished simply by shaking the mixture.

The stability of the two analytes in emulsions of unspiked gasoline, prepared with Triton X-100 and with CTAB was also evaluated and the results are shown in Fig. 1. In the CTAB-based emulsion both analytes were stable for at least 30 min and losses became significant after 45 min. The same was found for Cu in the Triton X-100-based emulsion; the only exception was

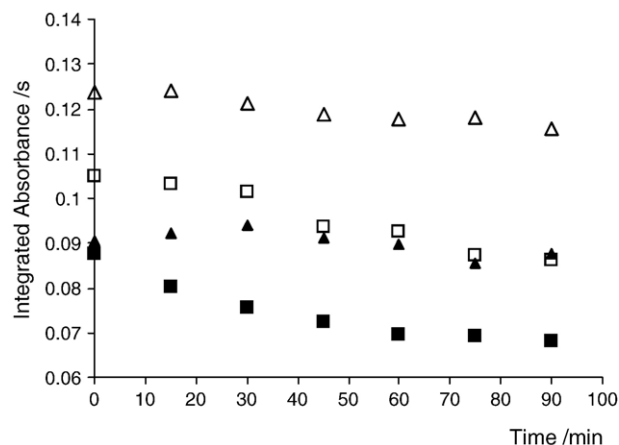


Fig. 1. Stability of Cu and Cr in a CTAB and Triton X-100-based unspiked gasoline emulsion. □ Cr in CTAB emulsion; ■ Cr in Triton X-100 emulsion; △ Cu in Triton X-100 emulsion; ▲ Cu in CTAB emulsion.

Cr in the Triton X-100-based emulsion for which losses occurred more rapidly. It might be assumed that these analyte losses would diminish when more concentrated acids were used in the emulsion preparation as proposed by Saint'Pierre et al. [3,9]. However, this approach has not been further investigated, as the long-term stability obtained under the selected conditions was sufficient for the current investigation.

3.2. Temperature program optimization

Pyrolysis and atomization temperature curves for Cr and Cu were established using an unspiked gasoline emulsion as shown in Fig. 2. The optimum pyrolysis and atomization temperatures were 700 and 2400 °C for Cu and 1300 and 2500 °C for Cr respectively. The time and temperature of the drying step and the atomization time were determined experimentally to provide optimum conditions. The gas flow was stopped during the atomization step and the cleaning step was fixed as recommended by the instrument manufacturer. The optimized temperature

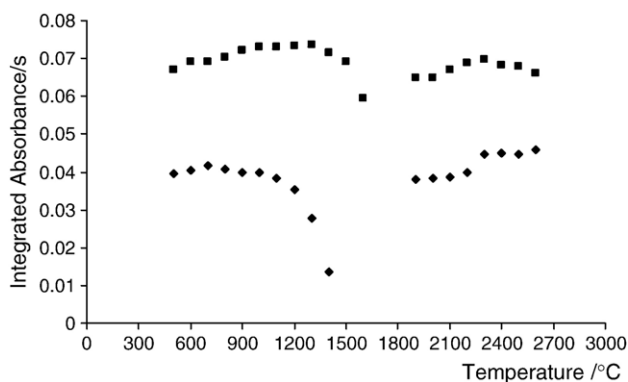


Fig. 2. Pyrolysis and atomization curves for Cu and Cr in a CTAB-based unspiked gasoline emulsion. ◆ Cu in CTAB emulsion; ■ Cr in CTAB emulsion.

Table 2
The graphite furnace temperature program

Element	Cr	Cu
	Temp.(°C)/ramp(s)/hold(s)	Temp.(°C)/ramp(s)/hold(s)
Drying 1	90/5/30	90/5/30
Drying 2	110/5/30	110/5/30
Pyrolysis	1300/5/30	700/5/30
Atomization ^a	2500/0/5	2400/0/5
Cleaning	2750/3/5	2600/3/5

^a No argon flow in this stage.

program for both elements in gasoline emulsions is shown in Table 2.

3.3. Analytical figures of merit and calibration

One of the principal problems associated with the determination of trace elements in gasoline and other petroleum products is the lack of knowledge about the form of the analyte in the sample, and that different forms might exhibit different sensitivity. The analyte addition technique provides compatibility among the calibration curves for different samples in terms of possible interferences; however, a pre-requirement for the use of this technique is that the analyte added to the sample behaves in the same way as the analyte originally present in the sample, which is not necessarily the case. Due to this, the feasibility of use aqueous standards for calibration was evaluated by the comparison with the analyte addition using metal–organic standards. Analyte addition using inorganic standards was discarded due the need for a higher amount of surfactant to provide compatibility between the aqueous solution and the emulsion.

The linear range and the slopes of the calibration curves obtained with aqueous solutions and with analyte addition using organic standards are shown in Table 3. As can be seen, they differ significantly, which implies that the analytes exhibit different behavior in the aqueous solution and in the metal–organic standards. Hence, the analyte addition technique using metal–organic standards was chosen for calibration. The feasibility of this approach has been investigated using an independent technique, as will be discussed in Section 3.4. The correlation coefficients of the chromium and copper calibration curves were close to unit within the investigated concentration range.

The LOD of each analyte was calculated as the analyte concentration corresponding to three times the standard deviation

Table 3
Figures of merit for the proposed method

Analyte	r^2	LOD ^{a,b} ($\mu\text{g L}^{-1}$)	RSD ^b (%)	Linear range ^c ($\mu\text{g L}^{-1}$)	Characteristic mass (pg)	Slope of calibration curve ($\text{L } \mu\text{g}^{-1}$)	
						Aqueous solution	Analyte addition
Cu	0.9990	5.0	6–9	3–45	20	0.0044	0.0023
Cr	0.9987	1.5	4–6	1–12	9.0	0.0113	0.0057

^a In the original gasoline sample.

^b $n=10$.

^c In the oil-in water emulsion.

Table 4
Concentration of metals in commercial gasoline samples

Sample	Cu ($\mu\text{g L}^{-1}$)		Cr ($\mu\text{g L}^{-1}$)	
	Emulsion	HCl extract	Emulsion	HCl extract
1	25.1±0.1	25.3±0.2	3.43±0.02	3.40±0.01
2	37.7±0.3	38.1±0.3	1.72±0.02	1.69±0.04
3	16.3±0.1	nd	2.34±0.04	nd
4	19.7±0.7	19.2±0.5	1.95±0.09	1.88±0.08
5	17.3±1.3	nd	2.54±0.17	nd
6	13.1±1.0	12.6±1.2	3.05±0.23	2.72±0.27

Mean±S.D.; $n=3$. nd = not determined.

for ten consecutive measurements of the emulsion blank, divided by the slope of the calibration curve. The sensitivity was evaluated by determining the characteristic mass based on the respective analytical curve. The precision calculated from ten consecutive measurements and defined as the relative standard deviation (RSD) of emulsions containing 5 and 15 $\mu\text{g L}^{-1}$ of the analytes was 9% and 6% for Cu and 6% and 4% for Cr, respectively. Spike recovery tests were employed to check the accuracy: known amounts of metal–organic chromium and copper were added to the gasoline samples which were prepared as CTAB-based emulsions, resulting in 5 and 15 $\mu\text{g L}^{-1}$ spikes in the emulsion. The recoveries were 90% and 94% for Cr and 95% and 98% for Cu, respectively.

3.4. Analysis of samples and validation

The method was applied for the determination of copper and chromium in commercial gasoline samples collected from different gas stations in Salvador, BA, Brazil; the results are shown in Table 4. The accuracy of the proposed method was evaluated by comparing the results with those that were obtained using a procedure developed by Kowalewska et al. [8]. Aliquots of the six commercial gasoline samples were gently heated to near-complete evaporation, with the purpose of analyte pre-concentration and matrix removal. Then, 2 mL of concentrated hydrochloric acid was added to the residue, and quantitatively transferred to a 10-mL volumetric flask. The volume was made up to the mark with deionized water and the resulting solution was analyzed by ET AAS using aqueous standards diluted with 20% (v/v) HCl for calibration. It was observed that the heating should be made carefully and under constant agitation, in order to avoid the impregnation of residues on the recipient wall. This procedure is obviously

limited to non-volatile analytes and has been applied with success for gasoline due the high volatility of the matrix.

For the samples 3 and 5 the acid dissolution after matrix evaporation has not been fully completed and the analytes could not be transferred quantitatively to an aqueous solution for the analytical measurement. The different chemical behavior of these samples, in terms of dissolution, might be attributed to the fact that gasoline is a quite complex mixture of several hydrocarbon fractions of variable chemical composition. The evaporation behavior might depend on the refining processes used and also on the nature of the petroleum from which it originated. The residue dissolution with HNO₃ was also evaluated; however the results were not satisfactory.

The concentration values obtained with the comparative method, which are also shown in Table 4, showed no significant difference from those obtained by the proposed procedure, for 95% of confidence. The results were also in accordance with those reported in recent publications for these elements in gasoline [3,4,8,9].

4. Conclusion

In this study, metal concentrations (Cr, Cu, Fe, Mn and Ni) in Triton X-100, SDS and CTAB were compared. These results must be used with care because metal concentrations can vary in accordance with the product manufacturers. The results indicated that the use of CTAB reduces the amount of surfactant required to prepare oil-in-water emulsions of gasoline. In addition, the use of higher proportions of gasoline in the emulsion also was possible, resulting in a lower dilution factor and improved limits of detection. The characteristic mass obtained for CTAB-based gasoline emulsions for Cu and Cr was higher than the values indicated in the equipment manual for 0.1% (v/v) HNO₃ solutions, 6 and 1.5 pg respectively, which confirms the different behavior of these analytes in aqueous and organic medium.

Finally, the emulsions prepared with CTAB remained stable over several days, and the sample remained evenly dispersed in the emulsion, avoiding any problem associated with inhomogeneity. Analyte losses from the emulsion were, however, observed already after 45 min, so that these losses might be the critical parameter. The use of CTAB might be of advantage also for the emulsification of other petroleum-based products for the determination of their trace metal content with atomic spectrometric methods.

This paper proposes the use of CTAB as surfactant for gasoline sample preparation as emulsions for the determination of Cr and Cu using ET AAS. The method is simple and does not require the sample to be subjected to any harsh or time-consuming treatment with concentrated acids, long-time heating or dilution with organic solvents, minimizing the risks of contamination or losses. In spite of the dilution inherent to this emulsion sample preparation procedure, the method has good sensitivity with detection limits sufficiently low for the concentrations of the metals observed in commercial gasoline samples. The use of SDS as surfactant also was evaluated, however due to its relatively high metal content its use was discarded.

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