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Determination of aluminum by electrothermal atomic absorption spectroscopy in lubricating oils emulsified in a sequential injection analysis system

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Abstract

The sequential injection (SIA) technique was applied for the on-line preparation of an "oil in water" microemulsion and for the determination of aluminum in new and used lubricating oils by electrothermal atomic absorption spectrometry (ET AAS) with Zeeman-effect background correction. Respectively, 1.0, 0.5 and 1.0 ml of surfactants mixture, sample and co-surfactant (sec-butanol) solutions were sequentially aspirated to a holding coil. The sonication and repetitive change of the flowing direction improved the stability of the different emulsion types (oil in water, water in oil and microemulsion). The emulsified zone was pumped to fill the sampling arm of the spectrometer with a sub-sample of 200 μl. Then, 10 μl of this sample solution were introduced by means of air displacement in the graphite tube atomizer. This sequence was timed to synchronize with the previous introduction of 15 μg of $Mg(NO_3)_2$ (in a 10 μl) by the spectrometer autosampler. The entire SIA system was controlled by a computer, independent of the spectrometer. The furnace program was carried out by employing a heating cycle in four steps: drying (two steps at 110 and 130 °C), pyrolisis (at 1500 °C), atomization (at 2400 °C) and cleaning (at 2400 °C). The calibration graph was linear from 7.7 to 120 μg Al l^{-1}. The characteristic mass (mo) was 33.2 pg/0.0044 s and the detection limit was 2.3 μg Al l^{-1}. The relative standard (RSD) of the method, evaluated by replicate analyses of different lubricating oil samples varied in all cases between 1.5 and 1.7%, and the recovery values found in the analysis of spiked samples ranged from 97.2 to 100.4%. The agreement between the observed and reference values obtained from two NIST Standard Certified Materials was good. The method was simple and satisfactory for determining aluminum in new and used lubricating oils.

Keywords: Sequential injection analysis; Lubricating oils; Emulsions; Electrothermal atomic absorption spectrometry; Aluminum; On-line analysis

1. Introduction

Trace elements in engine oils have received considerable attention in recent years because of the value of trace element data in understanding the oil performance under severe conditions. The determination of metals (such as: chromium, copper, iron, lead, tin and aluminum) in lubricating oils, particularly used motor oils, is important as a direct way to diagnose, estimate not-yet-visible wear in moving parts and even to implement maintenance programs for a variety of equipment [1]. In the treatment and regeneration processes of waste oils a precise determination of the metallic content is also paramount. In particular, when the level of aluminum goes up we can find out that the following engine components: certain types of bearings, bushings, pistons, blowers, washers, clutches and/or pumps are causing engine wear [3].

Also, since most modern engine blocks are made with aluminum alloys, aluminum can be found in lubricating oils

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as tiny solid particles or as oil-soluble compounds resulting from a chemical reaction with carboxylic acids produced by an uncompleted combustion of the fuel, or additives such as corrosion inhibitors contained in the lube oil [2]. Most lube oils contain detergents which are able to solubilize water in inverse micelles structures, hence aluminum might be also found under an ionic form in used lube oils [3].

Before analyzing the lubricating oils for different elements by instrumental techniques, it is important to prepare the oil sample in an appropriate form. Among different methods of sample preparation, dry ashing of oil is the most accurate method for total recovery of the elements [4]. However, wet and dry ashing techniques are time-consuming and inconvenient [5].

Other methods are:

(i) The direct dilution, in which the oil is diluted with an organic diluent [6]. The dilution of samples is required for the preparation of viscous samples to equalize samples of varying viscosity in order to obtain a proper instrumental response. However, while achieving these aims, the dilution also reduces the overall sensitivity of the analysis, degrades the limit of detection, and adds an opportunity for contamination or analyst error. Also, the direct analysis of viscous lubricating oil in a nonpolar solvent solution is not always a satisfactory technique for many reasons, such as the volatility and toxicity of the solvent or its corrosivity or agresivity on tubing and plastic parts [7].

(ii) Lengthy digestion procedures. The acid digestion treatments to pass the analytical sample in a water environment, eventually with the help of a microwave heating [8,9] are often tedious and not completely fool proof as far as the conservation of the sample is concerned.

(iii) The extraction into the aqueous phase [10,11]. This procedure is time-consuming and prone to poor recoveries.

Modern instrumental techniques such as atomic absorption spectrometry (AAS) [12–15], electrothermal atomic absorption spectrometry (ET AAS) [16,13] and inductively coupled plasma emission spectrometry (ICP AES) [8,14–18] have been widely used for the analysis of lubricating oils. However, the previously mentioned techniques require of considerable sample pre-treatment (usually several hours) increasing the risks of contamination and sample loss. As an alternative to the previously mentioned methods, the emulsification of oil samples or its solubilization in a microemulsion has been proposed [19,20]. Such emulsification methods introduce water in the conditioned samples and most often tend to simplify their handling in spectrometric analysis equipments, particularly in the spray/atomization injection devices.

Some articles have been published dealing with the dilution of edible [21] and motor [22] oils, and the direct [23] and on-line [18] emulsification of edible oils prior to the determination of aluminum (among other elements) either by and by ET AAS [21] or ICP-MS [18,23]. The on-line phase behavior of water-oil-surfactant (w-o-s) mixtures has been the subject of recently research [24–26]. Jiménez et al. [24] have determined Al (among other elements) in olive oils by ICP-MS with on-line preparation of their emulsion in a FI system. In the case of Jimenéz et al. [24] the optimization was limited to obtain a stable emulsion, to improve the sensitivity and reproducibility, and the absence of matrix interference. While, the “on-line” formulation of three-phase systems has only be recently reported in a work of our research group [25,26]. In this case the on-line phase behavior allowed the determination of chromium in lubricating oils in a FI system by ET AAS.

However, to the best knowledge of the authors the use of emulsions to determine aluminum in lubricating oils has not yet been reported by the literature. Based on the above given consideration, this paper discusses the analytical potential of an on-line sequential injection analysis (SIA) [27,28] system for aluminum determination by ET AAS in lubricating engine oils, comparing the results with those obtained from a traditional method too. The results established the optimum phase behavior formulation of surfactant/oil/water methodology with regard to a reduction of the time of preparation of these highly viscous samples. Stable micro-emulsions is the only requirement needed to use this methodology in order to allow a fast, precise and accurate procedure for the determination of aluminum in typical branched isoalkane based lube oils. It has been demonstrated that SIA is a very attractive approach for the on-line emulsification of lubricating oils and to determine chemical species in these kinds of samples.

2. Experimental

2.1. Instrumentation

All experiments were performed using an atomic absorption spectrometer Perkin-Elmer model 4100 ZL with Zeeman effect background correction and equipped with a Perkin-Elmer aluminum hollow cathode lamp operated at 15 mA. Pyrolitic graphite coated tubes were used with pyrolytic graphite coated graphite platforms. Measurements were carried out at a wavelength of 309.3 nm with a 0.7 nm slit. The integration time was of 3 s and three independent measurements were carried out as replicas. Nitrogen was used as protective inert gas. A Perkin-Elmer software 4100 PC (version 3.7) was operated to run the data analysis.

The SIA system was constructed from the following components: A Gilson Minipuls peristaltic pump with Solvaflex tubing (from Technicon, Tarrytown, NY, USA); a six-port selection valve (V) (Model TVV-6, Latek-Teflon-Motorventile, Eppelheim, Germany); A Sonicor SC-100TH ultrasonic bath; a time-based variable-volume injector (TBSI) [29,30] controlled by a programmable Gralab Model 900 electronic timer and Solvaflex tubing. All connections and mixing coils from V to SAA were made from 1.0 mm

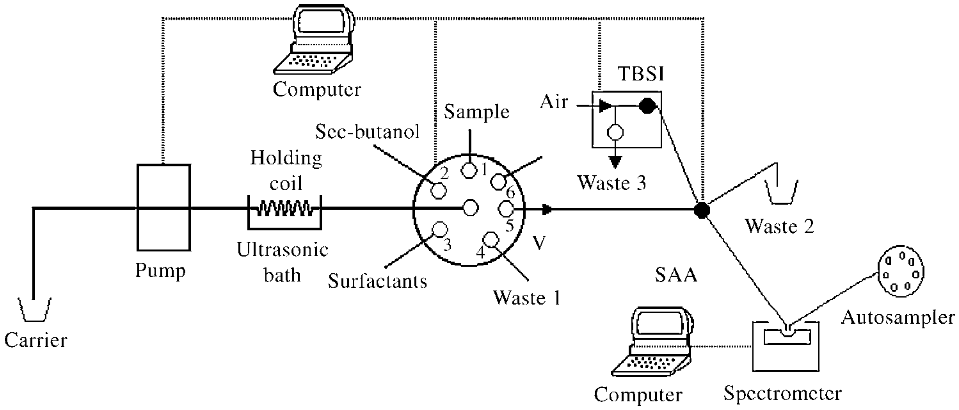

Fig. 1. Sequential injection manifold. TBSI = time based solenoid injector; V: six port rotary selection valve; SAA: sampling arm assembly.

i.d. tubing. A sampling arm assembly (SAA) allowed a quartz tube to be moved horizontally in and out of the waste vessel, graphite furnace and washing solution in order to introduce sample aliquots. The i.d. of tubing for the TBSI and SAA was of 0.5 mm. A TDK model 286 computer was interfaced with the pump, V, TBSI and SAA.

2.2. Reagents

All reagents used were analytical grade. N-heptane from Baker was certified >99%. Doubly deionized water through a Millipore system down to an 18 MΩ/cm resistivity, was used to make up solutions and for rinsing purposes.

A commercial Al standard (1.000 g l^{-1}, Merck) was use. All working solutions were prepared by serial dilution of the standard solution with a 1.5% (v/v) nitric acid solution immediately before use. A 65% (w/v) concentrated nitric acid (Riedel-de Haën, Germany) was used to prepared more diluted solutions of the acid.

Ethoxylated nonylphenols surfactants, with an average number of ethylene oxide groups per molecule (EON) of 4, 6 and 9 were supplied by Clariant GmbH. Intermediate ethoxylation degree was attained by mixing these surfactants on a molar concentration basis [31]. The EON is directly linked with HLB (hydrophilic–lipophilic balance [32]. All surfactants solutions were prepared to produce a 0.1% (w/v) of NaCl. Surfactants were introduced either as a heptane (EON = 4 and 6) or as an aqueous (EON = 9) solution at a concentration 50 g l^{-1}.

A modifier solution of magnesium nitrate at 1500 mg l^{-1} was prepared by dissolving 0.1297 g of $Mg(NO_3)_2 \cdot 6H_2O$ from Sigma in 50 ml of water.

2.3. Samples

A variety of eight new motor oils were purchased locally. Also, the same quantity of used oils was obtained from oil drained during regular changes of automobile engines. For the analysis of used lubricating oil samples the pre-treatment previously described was followed [25].

Table 1
Optimized experimental conditions

Parameter	Value
Microemulsion preparation	
Salinity (NaCl concentration of the aqueous phase)	0.1 w/v
EON	5.04
FI	
Sample volume	0.5 ml
Flow rate	2 ml min^{-1}
Holding coil length	3 m
Tubing length between P and V	5 m
Tubing length between V and SAA	1 m
Total tubing length	6 m
Volume of the surfactants mixture solution	1 ml
Volume of the sec-butanol solution	1 ml
ET AAS[a]	
Collected sub-sample volume	0.2 ml
Injected sub-sample volume	10 μl

[a] The optimized furnace temperature program was as given below.

2.4. Procedure

Samples or standard, sec-butanol and surfactants solutions were sequentially aspirated through their respective lines into the holding coil (HC) and then propelled by the peristaltic pump (P) at room temperature (20 ± 3 °C) as indicated in Fig. 1, under the optimized operating conditions given in Table 1. The SIA-ET AAS program was as described in Table 2.

Table 2
Temperature program for the graphite furnace

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Argon flow rate (ml min^{-1})
Drying	110	1	20	250
Drying	130	5	30	250
Pyroysis	1500	10	20	250
Atomization	2400	0	3 (without reading)	0
Cleaning	2400	1	2	250

2.4.1. Sequence 1

The sample, surfactants mixture and sec-butanol solutions were respectively aspirated during 30, 15 and 30 s. The duration of this sequence was 75 s.

2.4.2. Sequence 2

Once, the sample/surfactants/sec-butanol mixture reached the HC located in an ultrasonic bath, the pumping direction was reversed and forwarded four times for 15 s to form a homogeneous emulsified zone. The duration of this sequence was 60 s.

2.4.3. Sequence 3

Then the plug of emulsion was propelled by the carrier stream to fill the tubing of the sampling arm assembly (SAA), which was at its waste (W_2) position. When the emulsion plug tubing was filled completely (with a 200 μl sub-sample of emulsified sample), the injection valve (V) was turned to divert the flowing stream to waste (W_1) in order to prevent the build-up of high pressure in the tubing. The duration of this sequence was 90 s.

2.4.4. Sequence 4

This sequence was timed to synchronize with the spectrometer computer, which had been pre-programmed to introduce 10 μL aliquot of magnesium nitrate modifier previous to the introduction of 10 μL aliquot of standard or emulsion solution and to run the furnace temperature program (Table 1). The sequential and alternately activation of SAA (to the injection position) and the TBSI allowed the deposition of the aliquot of emulsion on the graphite tube platform of the atomizer, previous to the introduction the aliquot of standard or sample solution. The duration of this sequence was 90 s.

2.4.5. Sequence 5

The washing procedure was performed. For this, V and SAA were activated to successively pump the carrier solution to waste 2 (during 30 s) and waste 3 (during 20 s) in order to propel the emulsion plug to waste 2 and to wash the TBSI tubing, respectively. The duration of this sequence was 50 s.

2.5. ET AAS conditions

In order to optimize the drying, pyrolysis and atomization conditions, absorbance measurements were made for an aluminum standard solution of 50 $\mu g\, l^{-1}$ and an un-used lubricating oil.

Magnesium nitrate has been the most widely used modifier for aluminum determination by ET AAS [33]. Therefore, in this work, this modifier was used to stabilize aluminum during the pyrolysis step. The optimum temperatures of the drying step were studied in the range from 100 to 200 °C. The use of one drying step and temperatures above 150 °C lead to sample losses by splattering, therefore, it was necessary to include a second drying step (Table 1). The pyrolysis temperature was varied between 500 and 200 °C, using an atomization temperature of 2400 °C (as shown in Fig. 2). In both cases, the optimal pyrolysis temperature (T_{pyr}) that could be used without loss of aluminum was 1500 °C (Fig. 2). The determination of the optimum atomization temperature was carried out by stuying different atomization temperatures between 2000 and 3000 °C. Fig. 2 shows that the aluminum absorbance values increased in both cases to an atomization temperature of 2300 °C and then slightly decreased above 2500 °C. The optimized graphite tube atomizer drying, pyrolysis and atomization times and temperatures are given in Table 2.

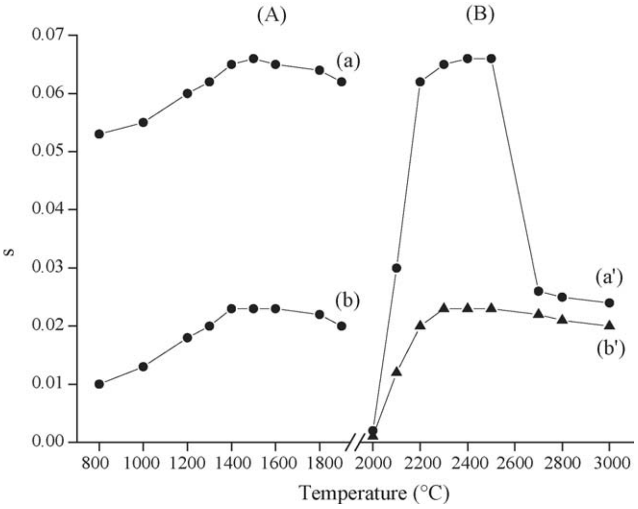

Fig. 2. Pyrolysis and atomization absorbance signals as a function of temperature. Pyrolysis (A) and atomization (B) temperatures; (a, a′) for a 50 $\mu g\, Al\, l^{-1}$ standard solution; and (b, b′) for a new oil sample. Experimental conditions as specified in Tables 1 and 2.

2.6. SIA variables

In the system described here, the precise instrument response at a given concentration of analyte in standard solution or of an oil sample is due mainly to the formation of a stable microemulsion-oil-water (mow), the dispersion of the sample plug, to the atomizer characteristics and to the response time of the detection/recording system.

In this work the SIA approach was found to be simpler than the previous reported flow injection (FI) system based on the merging-zones principle (injection in parallel into the flow system) with confluence points [25]. Particularly, the recirculation of solutions was avoided, the use of an additional volume based injection valve was not necessary, and a single line tubing connected the SIA system with the other instrumental components. It was evident, that a stable mow was formed here too due to an appropriate mixing of the components in the SIA system here proposed. Additionally, the SIA procedure facilitates the automation of the manifold.

Inner diameters of tubing, length of HC, pump speed and number of times that the sample/surfactants plug was forwarded and reversed (N) in the HC were found to affect the precision and the sensitivity of measurements. The best

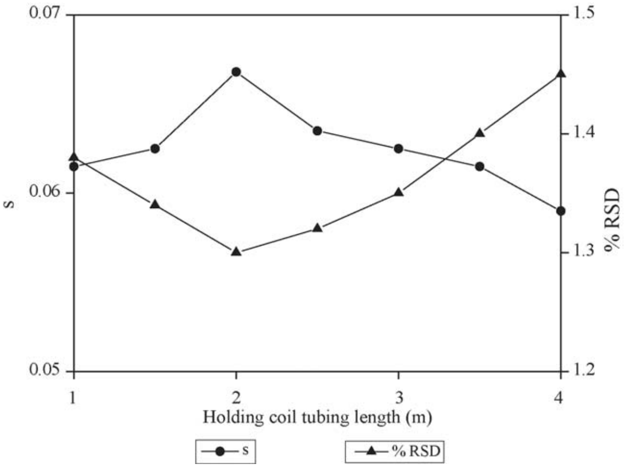

Fig. 3. Influence of holding coil tubing length on absorbance and percentage R.S.D. for a 50 μg Al l^{-1} standard solution; experimental conditions as specified in Tables 1 and 2.

precision was obtained with an inner diameter of 1 mm and this was chosen for further work. The precision deteriorated as the inner diameter was further increased. The results (Fig. 3) revealed that the precision increased as the tubing length increased to 2 m, but it decreased as the tube length increased above 3.0 m due to larger dispersion caused by the effect of the ultrasonic radiation. The pump speed should be 2.0 ml min^{-1}. Decreasing the total flow below 1.5 ml min^{-1} resulted in a significant consumption of time. Whereas, too high flow rates were inconvenient as a fast collection time made difficult the selection of an appropriate segment to be introduced for ET AAS evaluation. The alternative change of the flow direction of aspirated small slugs of sample and reagents inside the HC was found to facilitate the homogenization of the microemulsion. Therefore, multiple flow reversals with the same time periods from 4 to 20 s were then conducted to enhance the emulsification process. The optimum time for the flow reversals was 15 s for both, the forward and the reverse steps.

The length of tubing between HC and SAA did not greatly affect the reproducibility of the results. However, the length of these tubing was kept as short as the instrumental allowed in order to simplify the SIA system (see Table 1).

2.7. The three-phase transition of the water-oil-surfactant emulsified system

The correlation for the attainment of an optimal formulation with nonionic surfactacts (three-phase behavior) systems can be written [4] as:

$$\alpha - \text{EON} + bS - k\,\text{EACN} + \phi(A) + \delta\Delta T = 0$$

where α is a parameter proportional to the surfactant "tail", EON is the number of ethylene oxide groups per molecule of surfactant, S is the salinity of the aqueous phase expressed as weight percent of NaCl, EACN is the number of carbon atoms in the alkane molecule or a characteristic of the oil phase for a non alkane molecule (e.g., its equivalent alkane carbon number EACN), ϕ(A) represents the effect of both the type and concentration of alcohol, ΔT is the variation is the deviation from ambient standard temperature (25 °C), and b, k and δ are constants. The transition between phases (Winsor I or WI ↔ Winsor III or WIII ↔ Winsor II or WII; see below) are induced by changing one of the variables. When the crossing of optimum formulation induces a phase transition, the surfactact-rich mow phase undergoes a continuous change from oil phase (in WII systems) to water phase (in WI systems or vice versa, passing through the intermediate middle phase state in the WIII case. Since in our case, there is no variation of α, S (0.1 wt.% NaCl in the mixture of surfactants solution [34], ϕ(A) and temperature ΔT, the only remaining compensation is due to EON and EACN (effect of amount of oil). Therefore, in our case, the effects of the amount of oil (sample volume), salinity and EON were optimized systematically (changing one of the variables while keeping the other constants) in the SIA system. The phase behavior at equilibrium according to Winsor notation (I: surfactant in water, II: surfactant in oil, III: three-phase system) denotes the emulsion type. The Winsor I (respectively II) phase behavior takes place when the surfactant affinity for the aqueous (respectively oil) phase dominates, and most of the surfactant is located in the aqueous (respectively oil) phase, the other one being an excess phase with essentially no surfactant. Winsor type III phase behavior exhibits a microemulsion in equilibrium with both excess water and excess oil, and is associated with the occurrence of an extremely low interfacial tension, with an emulsified system generally composed of oil and water droplets dispersed in the microemulsion [35].

Table 3 shows the effect of the amount of oil (sample volume) on the phase behavior. Here, three different zones can be easily noticed. The first one (WI) is at sample volumes from 0.2 to 0.4 ml; a second zone (WIII) goes from 0.4 to 0.7 ml; and a third zone (WI) exists above 0.7 ml. By changing the amount of oil, an unidimensional formulation scan is attained which covers the different cases of phase behavior, i.e. Winsor type I, II or III [4,36], with the associated emulsion morphology, i.e., oil-in-water (O/W), water-in-oil (W/O) and oil-plus-water-in-microemulsion (O/W/M) respectively [4]. Due to the effective mixing of the components in the

Table 3
Effect of sample volume on phase behavior

Sample volume (ml)	Phase	
	New oil	Used oil
0.2	II	II
0.3	II	II
0.4	III	III
0.5	III	III
0.6	III	III
0.7	III	I
0.8	I	I
0.9	I	I
1.0	I	I

Table 4
Effect of EON on phase behavior

EON	Phase	
	New oil	Used oil
4.00	II	II
4.25	II	II
4.50	II	II
5.04	III	III
5.20	III	III
5.35	I	III
6.00	I	I
6.60	I	I
8.06	I	I
9.0	I	I

Table 5
Effect of sec-butanol concentration on phase behavior

Sec-butanol concentration (% v/v)	Phase	
	New oil	Used oil
0	II	II
1	II	II
2	III	III
3	III	III
4	III	III
5	I	I
6	I	I
7	I	I
8	I	I
9	I	I

SIA system here described, the sensitivity increased with sample volume, but only reproducible results were obtained when Winsor WIII type emulsion was obtained. A sample volume of 0.5 ml was found to be a good compromise to obtain a Winsor type emulsion for both, new and used oils.

Table 4 indicates that at low EON (EON <5) the surfactant mixture is essentially lipophilic and the systems split into two phases, a mow oil phase which contains most of the surfactant in micellar-like structures and an excess aqueous phase in the absence of surfactant [4]. For EON >6, the surfactant is mostly in the aqueous phase in a micelle/mow structure, in equilibrium with an oil phase which essentially contains no surfactant [37,38]. At EON values between 5.20 and 5.35, a three phase behavior is exhibited for new and used oils, with most of the surfactant present in the mow middle phase, which presents a complex bicontinuous structure with domains similar to normal and inverse micelles, in equilibrium with excess oil and water phases which do not contain a significant amount of surfactant [39]. Hence any aluminum found in the water phase must be in ionic form, and any found in the oil phase as an organic compound, with a mixture of both in a mow.

2.8. Stabilization of the microemulsion

Provided that there is enough surfactant, the mow WIII with both oil and water minidrops were obtained. However, the system exhibited a poor stability producing larger drops of oil and become turbid. The drops, particularly the oil droplets, were likely to coalesce because of the low stability of emulsified WIII systems. The coalescence rate was too fast (ca. 30 s), which was highly inconvenient for the analytical aims of our work. In a previous work of our research team, the addition of a co-surfactant promoted the formation of three phases and it was closely related to the surfactant concentration. Therefore, in this occasion, the same co-surfactant (sec-butanol) was introduced (Fig. 1). The effect of sec. butanol concentration of phase behavior is shown in Table 5. The introduction of a 3% v/v sec-butanol solution allowed the formation of a stable (for at least 1 month) WIII system with a low tension situation and the formation of small droplets.

Since the SIA manifold works as a single line system, in which the mixing of all components is made mostly through axial dispersion, it was difficult to perform a complete penetration of the sample plug with the reagents zones. Thus, an appropriate mixing of all the components was necessary to obtain a stable WIII system. Otherwise, the components of the mow progressively (in about 4 min) separated into two liquid layers due of a nucleation process of the oily phase and lead to inaccuracy of measurements if the emulsification process was not completed. When the HC tubing was placed in an ultrasonic bath, the mwo remained constant to allow the aluminum determinations in the SIA system here proposed. Therefore, ultrasonic radiation was subsequently used in all experiments.

2.9. Analytical figures of merit and application to real samples

A calibration graph was constructed with the aqueous standards (0–140 μg Al l^{-1}) in three replicates. The absorbance increased linearly with aluminum concentration as expressed by the equation $A_{\mathrm{Al}} = 0.0018 + 0.0013$ [Al], $r = 0.9991$ (for ten points calibration graphs), for the range 7.7–120 μg Al l^{-1} in aqueous solution, where A_{Al} represents the integrated absorbance values and [Al] corresponds to aluminum concentration in μg Al l^{-1}. The limit of detection was taken as three times the standard deviation of the blank signal was 2.3 μg Al l^{-1} ($m_o = 33.2$ pg). This detection limit was similar to those found using ET AAS (2.8 μg l^{-1}) [39], tungsten coil ET AAS (2.0 μg Al l^{-1}) [40], and inductively coupled plasma mass spectrometry (ICP-MS) (1.8 μg l^{-1}) [41]. The reproducibility (% RSD) for five independent measurements using 10 and 100 μg Al l^{-1} was 1.4 and 1.3, respectively. Similar precision was observed when real samples were evaluated. The reproducibility was 1.5 and 1.7% for the determination of aluminum in a new and a used oil sample, respectively.

In order to study the possible matrix interference on the aluminum absorbance, a standard addition graph was prepared by adding various amounts of Al (from 5 to 60 μg Al l^{-1} in a new oil sample. The equation obtained for the standard addition curve was $A_{\mathrm{Al}} = 0.0270 + 0.0014$ [Al],

$r = 0.9990$. The slope of this curve did not show a significant difference with that obtained for a single calibration curve ($P < 0.005$), which suggested the absence of any matrix effect.

Some assessment of the recovery of aluminum was made by adding 10 and 20 μg Al l^{-1} to a new lubricating oil. The recoveries values were of 97.2 and 100.4%, respectively. The accuracy of the method was further checked by determining the aluminum content in certified materials. Respectively, the results obtained were 123.4 ± 2.0 and 374 ± 3.0 μg Al l^{-1} in the NIST 1084a and 1085b certified materials, following the procedure described here. These results were in good agreement with the reference values of 126.5 and 370.2 ± 11.4 μg Al ml^{-1} (respectively, 104 and 304.4 ± 9.3 mg Al kg^{-1}) for the 1084a and 1085b materials, respectively. It should be pointed out that when the aluminum concentration was above the working range, the samples were diluted in hexane previous to their introduction in the SIA system.

2.10. Application to real samples

Using the SIA–ET AAS procedure previously described eight new and used oil samples were analyzed. Respectively, the amounts of Al found in new and used oils were 17.5 ± 1.5 μg l^{-1} or 21.8 ± 1.8 ng g^{-1} (in the range from 15.0 to 18.6 μg l^{-1} corresponding to 18.7–22.3 ng g^{-1}), and 170.1 ± 10.2 μg l^{-1} or 178.6 ± 10.7 ng g^{-1} (in the range 163.5–187.0 μg l^{-1} corresponding to 171.6–196.3 ng g^{-1}). The levels of aluminum found in this work for used oil samples were higher than those found in unfiltered used aircraft lubricating oils: 150.0 mg l^{-1} [2] and 25–45 mg l^{-1} [42], and in a used motor oil (80.6 mg l^{-1}) [43]. These different values can be attributed to the various types of wear and metal particles produced in the oil-wetted mechanisms.

3. Conclusions

The proposed on-line SIA automated method for the emulsification of oil samples and the determination of aluminum by ET AAS has proved to be sensitive, simple, reliable and reproducible. The SIA approach automated the oil sample manipulation, thus it drastically reduces the time of the “in-batch” preparation of the emulsified system containing nonionic surfactant, oil, water and alcohol. Also, similar SIA systems to that presented here could be adapted to other detection techniques, like: ICP, ICP-MS and spectrophotometry.

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