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Application of a fractionary factorial design to the determination of tin in lubricating oils by continuous flow hydride generation-atomic absorption spectrometry

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Abstract The determination of wear metals and metalloids in used lubricating oils allows the prediction of equipment failure. A number of procedures to determine wear metals in lubricating oils by atomic spectrometry has been published. Industry has lately shown a special interest in the determination of tin, since its appearance at certain levels in used oils indicates severe engine wear. Therefore, a method for the determination of the total tin content in used lubricating oils by hydride generation-atomic absorption spectrometry (HG-AAS) is described. Unused marine lubricating oils spiked with the analyte were digested in closed vessels in a microwave oven and the diluted product was used for continuous stannane generation. There are many factors that influence effective SnH_4 generation; therefore, fractionary factorial design was used to obtain an adequate sensitivity and also to stabilize the signal. Six variables were taken into account and a 2^{6-2}_{IV} design was used with spiked samples containing 30 ng g^{-1} Sn. The reproducibility, stability, calibration curve and limit of detection were established. The method was applied to different kinds of used lubricating oils. In all cases, the results were higher than those obtained in the industry by simple dilution.

1 Introduction

The diagnosis of engine state based on the determination of “wear metals” in used lubricating oils has been widely applied, and various procedures can be found in the literature[1–3]. However, little attention has been paid to semimetallic elements such as Sn and Sb that can also appear as “wear elements” coming from bearings in used lubricating oils. In fact, no publications devoted to the development of a special method for Sn has been described, in spite of routine analysis for Sn carried out by the oil industry. This may be due to the fact that tin is a problematic analyte element at ultratrace levels [4] and that hydride generation is required. Some oil supplier companies have lately developed an interest in Sn determination. Although the interpretation of results from wear metal analysis is sometimes confusing there is clear evidence of severe engine wear when tin is found[1]. Often, wear metals are found but no Sn, and its presence obviously depends on the metallic composition of the engine and its wear state. This determination is of special interest for used marine lubricating oils from high-power crossgear engines, since these oils are not changed (only purification and small additions are carried out), and therefore the engine history can be followed by periodic oil analysis.

In industry, the routine analysis of wear metals and semimetals is performed by simple dilution with kerosene followed by multielemental determination by inductively coupled plasma atomic emission spectrometry (ICP-AES). However, the total concentrations are not determined by this procedure [5]. Since methods that determine the total concentration of wear elements may be able to prevent engine failure, an accurate and precise method to determine the total Sn concentration in used lubricating oils was necessary. Such a method is presented in this paper. Samples are digested in a microwave oven, and the Sn is determined by HG-AAS. The silica tube atomizer exhibited unsteady signals as reported by others [4, 6]. This problem was first solved by repeated application of a standard solution before each Sn measurement. As many variables influence effective stannane generation, the optimization of one variable at a time can lead one to miss the most appropriate conditions, apart from being a tedious procedure. Fractionary factorial design [7] was used to obtain adequate sensitivity and to stabilize the signal. With this statistical technique it was possible to establish the most relevant factors that influence the signal values

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[1] CEPSA (Spanish Oil Company) private communication (1998)

and their possible interaction, using a reduced number of experiments. The experimental design was 2^{6-2}_{IV}. It was implemented with unused oils spiked with Sn in the presence of other elements that are found in marine lubricating oils and that are prone to give interferences. The method was then applied to used lubricating oils from marine engines and to other lubricating oils.

2 Experimental

2.1 Instrumentation

The digestion of the oils was carried out in a microwave oven CEM MDS. 2000, equipped with Teflon vessels PFA (120 mL, 1516.8 10^3 Pa). The determinations were performed with a Unicam 929 AA spectrometer equipped with a Unicam VP 90 vapor system and a silica tube atomizer.

Haake E 1, cryogenic bath.

Selecta, ultrasonic bath.

2.2 Reagents

Nitric acid, 70% (Panreac; p.a.), hydrogen peroxide, 30% (Panreac; p.a.), sodium borohydride (Panreac; p.a.), sodium hydroxide pellets (Merck; p.a.).

2.3 Sampling

Samples were obtained from a high-power crossgear engine while the engine was running and hot to obtain homogeneous and representative samples, they were stored in poly(propylene) bottles at room temperature.

2.4 Procedure for used oil

2.4.1 Analytical method. One gram of used oil was weighed into each perfluoroalkoxy (PFA) digestion vessel. The analytical method consisted of four stages (Table 1) and has already been described elsewhere for wear metals [2, 8]. The digestion product was diluted to 25 mL with distilled water (if an organic residue was formed, it was separated from the solution). A small volume (depending on the Sn concentration expected) of this solution was diluted to 50 mL with distilled water, to attain a pH of between 0.4 and 0.8. The sample was then taken to the continuous hydride generation system. Solutions of 1% (w/v) $NaBH_4$ in 0.5% (m/v) NaOH and a solution of 0.16 M HNO_3 were also used. The instrumental conditions were: sample flow rate and acid flow rate: 8 mL min^{-1}; $NaBH_4$ flow rate: 2.5 mL min^{-1}; argon flow rate: 400 mL min^{-1}; acetylene flow rate: 0.9 L min^{-1}; wavelength: 224.6 nm without background correction. The standards were prepared from unused oil spiked with tin and treated in the same way as the used oil. When the same type of unused oil was unavailable the standard addition method was used.

Table 1 Microwave program for 1 g of lubricating oil (for three reactors)

Stage	Reagent added	Time (minutes)	Power (%)[a]	Pressure (psi)[b]
1	10 mL HNO_3 (c)	10	20	50
2	5 mL HNO_3 (c)	10	30	40
		10	30	80
		10	40	125
		10	40	200
3	5 mL HNO_3 (c)	15	50	150
		15	60	180
4	5 mL H_2O_2	10	60	150
		10	60	170
		10	60	180

[a] 100% power = 630 W

[b] 1psi = 6.894757H × 10^3 Pa

2.4.2 Experimental design. The study was performed with digested unused oil, spiked with 30 ng g^{-1} tin. A fractionary factorial design at two levels (2^{6-2}_{IV}) was used. The main variables were parameters with no or little interaction. The two additional variables were associated with some second order interactions. Each experiment was performed three times.

3 Results and discussion

3.1 Preliminary test and sample preparation

Three different reagents described in the literature [9–16] were prepared to test stannane formation and subsequent Sn detection: metallic tin dissolved in HNO_3(c), $SnCl_2 \cdot 2H_2O$ dissolved in HCl(c) and a 4000 μg g^{-1} $SnCl_4$ Titrisol solution. With the first two reagents, stability problems were found. When Titrisol standard reagent of 4000 μg g^{-1} in $SnCl_4$ diluted to 2000 μg g^{-1} in 6% HCl was used, the solution was stable and this reagent was chosen for subsequent investigations.

Sample preparation was carried out by acid digestion in closed reactors in a microwave oven, taking into account the possibility of formation of volatile tin compounds, based on a method previously developed by us to analyze wear metals in lubricating oils [2]. One gram of unused oil was weighed and spiked with 0.25 mL of a 150 μg g^{-1} tin solution. The main modification consists of the dilution of the digestion product to 25 mL with distilled water (in the method developed previously, 1,4-dioxan was used for this purpose). At this point, a small amount of solid residue appeared on the solution surface. This residue was soluble in organic solvents, mainly in isobutyl methyl ketone and in strong basic aqueous medium. It could be separated very easily because it had a strong affinity to the plastic stopper of the flask. It was checked that no tin was lost in this step. The color of the sample (from green to yellow) after digestion was due to the presence of different amounts of nitrogen oxides with no influence on the final results. After diluting to 25 mL, the Sn concentration was 1.5 μg g^{-1}. As is known, the hydride generation technique is very sensitive (ng g^{-1} are detected), and therefore a further dilution must be carried out. In this case, 1 mL was diluted to 50 mL.

3.2 Variable screening for tin determination

The variables that could influence the tin determination by means of HG-AAS were identified in preliminary tests. The present study was performed with spiked and digested samples containing 30 ng g^{-1} tin concentration.

Since the signal was not stable enough, the atomizer was pre-conditioned by repeated application of the working solution until acceptable relative standard deviation (RSD) values were obtained [17].

3.2.1 Influence of dilution agent. HCl is most frequently used for covalent hydride generation [9, 17–21]. Other acids such as HNO_3 [9, 19, 21–23], H_2SO_4 [15, 19, 21, 22] and $HClO_4$ [22] have also been used with success. The choice of acid was influenced by the acid used during sample preparation. In our case, HNO_3 was used for the sample digestion. Therefore, dilute HCl and dilute HNO_3 were tested to dilute 1 mL of the digest. Higher absorbance values were obtained with HNO_3. The acid concentration is one of the variables that can greatly influence stannane generation, since the optimum acid range for an efficient reaction is very narrow [10]. On the other hand, the acid concentration is related to the concentration of the reducing agent [4]. The [borohydride concentration + sodium hydroxide concentration/acid concentration] ratio must be approximately equal to one, to obtain maximum yield [24]. In our case, the absorbance signal was adequate when this ratio was equal or slightly less than one.

3.2.2 $NaBH_4$ concentration. Typical concentrations of the reducing agent employed in HG-AAS for continuous flow systems are less than or equal to 1% [17, 18]. Higher concentrations produce foam which results in signal fluctuations. 0.1% (w/v), 0.5% (w/v) and 1% (w/v) (in 0.5% (w/v) NaOH) were tested with good results to keep the above-mentioned optimum ratio with the acid concentration. The optimum concentration of $NaBH_4$ for an acid concentration of ca. 0.16 M is 0.4% (w/v).

3.2.3 Argon flow rate. When the flow rate is high the hydride residence time in the atomizer is low; when the flow rate is low this time increases [18], but the stannane can decompose due to its instability. The best results were obtained at 300 mL min^{-1}. With higher flow rates, the absorbance signal was weaker.

3.2.4 Acetylene flow rate (atomizer temperature). The atomization temperature is one of the main factors in the determination of tin by HG [4]. Optimum atomization was obtained above 900 °C [25] with acetylene flow rates of 0.9 L min^{-1}.

3.2.5 Background correction. Measurements carried out at the principal wavelength with and without background correction resulted in the same absorbance signals. Thus, no background correction needed to be applied.

3.2.6 $NaBH_4$ and sample flow rate. For the continuous flow apparatus used the $NaBH_4$ flow rate can vary from 2.5 to 3.5 mL min^{-1} and the sample flow rate from 6 to 8 mL min^{-1}.

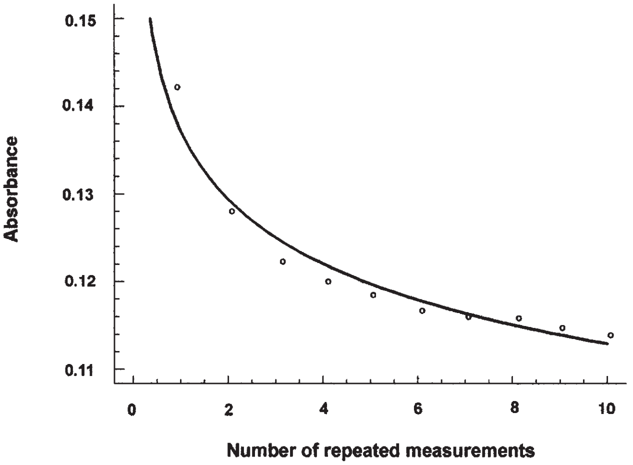

Fig. 1 Variation of the absorbance vs. number of repeated measurements

3.2.7 Influence of the quartz surface on hydride atomization. It is evident and well documented that frequently-used quartz cells are contaminated with sample components, or hydride-forming elements that may form a layer on the cuvette surface even after a single measurement [26]. We observed signal instability (high RSD values) together with a tendency of the signal to decrease, although the sensitivity obtained was sufficient to determine wear tin in lubricating oils. To stabilize the signal the silica tube was heated by flame at 900 °C for 15 min, since the high temperature causes structural changes [26]. Another treatment (already tested by other authors) is the immersion of the tube in a 40% HF solution [27] for 15 min and coating with 1% (m/v) $LaCl_3$. Repeated measurements of a spiked digested oil containing 30 ng g^{-1} Sn showed that the stability problem had not been solved by either treatment.

Finally, a pre-conditioning treatment by repeated application of the above-mentioned tin solution was tested with a new silica tube and with an old one using the following conditions: 1% (w/v) $NaBH_4$ in 0.5% (w/v) NaOH; 0.4 M HNO_3; 8 mL min^{-1} sample flow rate; 3 mL min^{-1} $NaBH_4$ flow rate; 300 mL min^{-1} argon flow rate; λ: 224.6 nm, without background correction. The signal was slightly higher with the new tube. However, after repeated measurements with both tubes, the signal decreased slowly together with the RSD value. It was also observed that when the RSD value was acceptable (< 2%) the signal was sufficiently stabilized. These results are shown in Fig. 1. Therefore, the working solution was measured several times until an RSD value under 2% was obtained.

3.2.8 Interferences. Stannane generation techniques can be affected by interferences from transition metals [4]. Therefore, the possible interferences from Fe, Mn, Cu, Cr, Cd, Ni, Zn and Pb were studied taking into account the metallic composition of the lubricated. Four samples were prepared with digested new oil and spiked with 30 ng g^{-1} tin and the metals at various tin/metals ratios. They were measured under the same conditions described in 2.6.7 after stabilizing the signal. The concentrations of tin and metals are shown in Table 2. Only when the tin/metals ra-

Table 2 Results of the interferences study for 30 ng g^{-1} Sn

Sn/metals ratio	Absorbance	
	Peak height	Peak area
1/ –	0.135	4.911
1/ 2	0.140	5.065
1/ 5	0.137	4.998
1/10	0.130	4.703

tio is 1/10 is a slight signal depression obtained. As this situation is unlikely in the oils under investigation, no interferences in the tin determination were to be expected and therefore, no masking agents were needed. However, the studies were performed on oils spiked with twice the metal concentrations to avoid possible interferences.

3.3 Factorial design for estimation of optimum conditions

A factorial design which took into account the number of variables influencing the signal was employed [28, 29]. The aim was to obtain an adequate signal for the wear tin determination, to try to stabilize the signal, avoiding cell preconditioning, and to obtain information about the interrelationships(interactions) between variables. Some variables were fixed as described in former sections, e.g., dilution with HNO_3 of the digested samples and the use of the principal wavelength without background correction. Based on the literature and on preliminary tests, a linear relationship between the variables chosen for the design and the response in the range studied was assumed.

This study was carried out with digested unused oils spiked with 30 ng g^{-1} tin and 60 ng g^{-1} of the metals studied as possible interferences. In order to evaluate the influence of the variables selected for the design on the signal, several repeated measurements were carried out. The six variables taken into account in the experimental design are listed in Table 3. A 2^{6-2} (resolution IV) fractional factorial design was chosen due to the high number of variables; this means that 16 experiments (1/4 of the complete factorial) were carried out [7]. The study was performed with three replicates of each experiment. The field variables (+) and (–) were fixed according to the study as described in 2.6 (Table 3).

The design was constructed by first considering a complete factorial design of the 4 principal factors. Then, two additional columns (corresponding to the two remaining variables) were added with third order interactions. Since our design has a resolution IV, the principal effects are not confounded; however, second order interactions are confounded between them [30]. The variables that are usually selected as principal factors are those where no or little interaction between them is observed [31]; in this case: acid concentration, $NaBH_4$ concentration, acetylene flow rate and inert gas flow rate. The additional factors were: sample flow rate and $NaBH_4$ flow rate. They were associated with the third order interactions 123 and 234 respectively.

Table 3 Experimental field definition

Factor	Symbol	Low level (–)	High level (+)
(1) HNO_3 concentration (mol L^{-1})	[HNO_3]	0.16	0.4
(2) $NaBH_4$ concentration (%)	[$NaBH_4$]	0.4	1
(3) C_2H_2 flow rate (L min^{-1})	Φ_{C2H2}	0.9	1.3
(4) Ar flow rate (mL min^{-1})	Φ_{Ar}	200	400
(5) Sample flow rate (mL min^{-1})	Φ_{Sample}	6	8
(6) $NaBH_4$ flow rate (mL min^{-1})	Φ_{NaBH_4}	2.5	3.5

Table 4 Experimental matrix

Experiment n°	Levels					
	Main factors				Additional factors	
	(1) [HNO_3]	(2) [$NaBH_4$]	(3) Φ_{C2H2}	(4) Φ_{Ar}	(5) Φ_{Sample}	(6) Φ_{NaBH4}
1	–	–	–	–	–	–
2	+	–	–	–	+	–
3	–	+	–	–	+	+
4	+	+	–	–	–	+
5	–	–	+	–	+	+
6	+	–	+	–	–	+
7	–	+	+	–	–	–
8	+	+	+	–	+	–
9	–	–	–	+	–	+
10	+	–	–	+	+	+
11	–	+	–	+	+	–
12	+	+	–	+	–	–
13	–	–	+	+	+	–
14	+	–	+	+	–	–
15	–	+	+	+	–	+
16	+	+	+	+	+	+

Abbreviations see Table 3

Table 5 Calculated average responses

Experiment n°	Peak height[a] $x \pm t(s/\sqrt{n})$	Peak area[a] $x \pm t(s/\sqrt{n})$
1	0.073 ± 0.012	2.601 ± 0.173
2	0.084 ± 0.003	3.056 ± 0.081
3	0.100 ± 0.006	3.570 ± 0.171
4	0.106 ± 0.001	3.961 ± 0.008
5	0.096 ± 0.009	3.626 ± 0.291
6	0.041 ± 0.002	1.459 ± 0.036
7	0.095 ± 0.002	3.505 ± 0.169
8	0.094 ± 0.002	3.279 ± 0.184
9	0.096 ± 0.007	3.409 ± 0.201
10	0.125 ± 0.055	4.722 ± 2.075
11	0.124 ± 0.001	4.620 ± 0.111
12	0.106 ± 0.007	3.870 ± 0.239
13	0.082 ± 0.002	2.981 ± 0.092
14	0.051 ± 0.019	1.640 ± 0.054
15	0.089 ± 0.011	3.030 ± 0.043
16	0.123 ± 0.002	4.491 ± 0.348

[a] Height or area units

Table 6 Effects on the two responses studied

Evaluation of effect		
Origin of effect	Peak height	Peak area
(1)[HNO_3]	–0.0029	–0.1062
(2) [$NaBH_4$]	**0.0235**	**0.8556**
(3) C_2H_2 flow rate	**–0.0180**	**–0.7264**
(4) Ar flow rate	0.0134	0.4614
(5) Sample flow rate	**0.0215**	**0.8569**
(6) $NaBH_4$ flow rate	0.0084	0.3413
12 + 35	0.0083	0.3249
13 + 25	–0.0103	–0.4583
14 + 56	0.0066	0.2805
24 + 36	–0.0015	–0.0376
34 + 26	–0.0088	–0.3970
45 + 16	0.0067	0.3563
23 + 15 + 46	–0.0092	0.2972

Significant effects in bold type

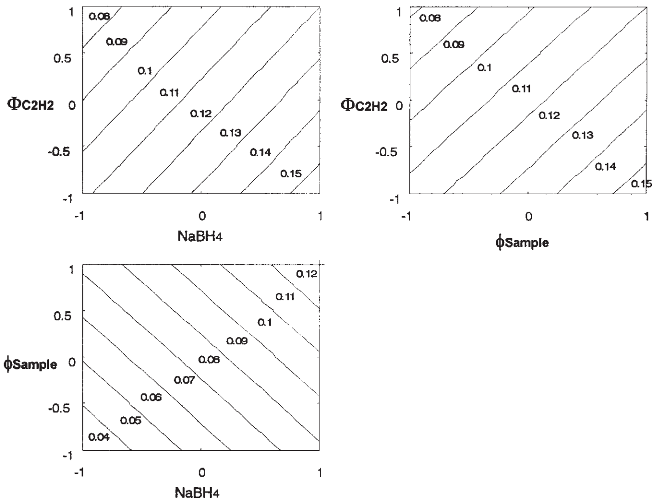

Fig. 2 Iso-response curves for peak height

The matrix is described in Table 4. Three replicates were prepared for each of the 16 experimental conditions shown in Table 4.

The experimental results (absorbance in height peak and in area) are displayed in Table 5. They are the means of each three replicates and they were processed with the statistical software "STATISTICA version 4". The estimated effects for each variable and for the interactions between two variables are shown in Table 6. After the second order, the interactions were considered to be insignificant.

An analysis of variance (ANOVA) showed that there are only three variables with a significant (95%) influence on the signal. They are: $NaBH_4$ concentration, acetylene flow rate and sample flow rate (p-values 0.05). The estimated effects for the interaction of two variables do not show significant differences in the response values both for peak height and for area. It is thus not necessary to resolve the confoundings between the interactions of two variables. The $NaBH_4$ concentration and the sample flow rate have a positive influence and the acetylene flow rate a negative influence on the signal. The other variables do not have a significant effect on the field studied. Thus, the absorbance signal can be represented by the following equation:

$$\text{Abs (area)} = 3.36 + 0.86\,[NaBH_4] - 0.73\,\Phi_{C2H2} + 0.86\,\Phi_{sample}$$

$$\text{Abs (peak height)} = 0.093 + 0.024\,[NaBH_4] - 0.018\,\Phi_{C2H2} + 0.021\,\Phi_{sample}$$

where the $NaBH_4$ concentration, Φ_{sample} and Φ_{C2H2} take the values +1 or –1 according to the experimental matrix (Table 4). The variables in our system behave in a linear way. The responses calculated from these equations are very close to the experimental average responses, and support the validity of the model. The iso-response curves for peak height are plotted in Fig. 2. The results obtained indicate that the sign combination +, –, +, which establishes the $NaBH_4$ maximum concentration, minimum acetylene flow rate and maximum sample flow rate, will give an optimum absorbance signal (inside the variation field established). Experiments 3 and 11 from the matrix were performed under these conditions, enabling the linear response variation, with the analyte concentration to be studied.

In order to establish the calibration graph, a set of standards from 3 to 100 ng g^{-1} was prepared and measured under conditions corresponding to experiments 3 and 11. The preconditioning of the cell was carried out with the 30 ng g^{-1} Sn solution before each standard solution was measured. The fitting to a straight line was better under experimental conditions 11, therefore, these working conditions were preferred. The standard set was also measured without preconditioning of the cell, and, since the response was stable, it was found that cell stabilization was not necessary for the conditions corresponding to experiment 11. The linear working range was from 3 to 50 ng g^{-1}. Thus, the aims of the experimental design were achieved and a procedure established with the conditions corresponding to experiment 11 and without preconditioning the cell.

With the aim of applying the method to used lubricating oils, the performances were determined. The detection limit was 2 ng g^{-1} (it was taken as the tin concentration in the unused oil giving an absorbance equal to that of the blank plus three times its standard deviation). The linear working range was from 3 to 50 ng g^{-1}. A 2.3% RSD deviation was obtained for 11 determinations of spiked lubricating oils containing 30 ng g^{-1} tin. The stability of several samples was determined by periodical measurements. It was found that the digestion product was stable for at least 1 month. However, after dilution it was only stable for three days.

3.4 Wear tin determination in used lubricating oils

A sample of used marine lubricating oil containing wear metals was analyzed by the proposed method. The stan-

Table 7 Concentration of tin in used lubricating oils

	Simple dilution with kerosene[a] (μg g^{-1})	Proposed method[b] (μg g^{-1})
Mobilgear 627	11	33.6
Mobilgard 412	12	48.3
Superciclope 150	17	71.3
SAE 90	11	30
Mobilgard 300	19	40
HP 320	35	108

[a] Results supplied by CEPSA Spanish oil company
[b] Mean of two determinations

dards for the calibration graph with the same type of unused oil and the sample were prepared as described in Section 2. In this case, three different aliquots (0.5, 1 and 2 mL) of the digested product were taken and diluted to 50 mL with distilled water. The absorbances obtained for the three aliquots of the sample were very similar to those obtained for the three corresponding blanks (prepared with unused oil and digested). Finally, both blank and sample were spiked with tin to obtain 50 ml of 30 ng g^{-1} Sn. In this case also, the signals obtained were very similar. In this way, we tested that the method was adequate for used lubricating oils, although the analyzed sample did not contain tin as wear element from the engine, in spite of containing wear metals.

Subsequently, some lubricating oil samples supplied by "CEPSA Spanish oil company" were analyzed. The method used in industry for wear element determination is simple dilution with kerosene (1 : 10) and ICP-AES. Obviously, the results obtained are useful for periodical oil analysis, but the total element content is not analyzed. Therefore, higher results were expected with the method proposed. The samples of three different oil types (Mobilgear 627, Mobilgard 412 and Superciclope 150) were taken from marine engines. The calibration graph method was used to determine the tin concentrations and the results are shown in Table 7. The proposed method was also applied to lubricating oils (SAE 90, Mobilgard 300 and HP 320) from other types of machinery (rowlock, gear, gearbox) also supplied by "CEPSA Spanish oil company". In this case, the corresponding unused oils were not available to prepare a calibration graph and the standard addition method was used. The results are also shown in Table 7. In both cases the results obtained are higher with the proposed method. It is worth noting that the differences are higher when the concentration increases.

4 Conclusions

The proposed method enables the determination of the total tin content in lubricating oils. It permits an early diagnosis of the engine state compared to the simple dilution method. In developing an analytical method to determine hydride-forming elements, an experimental design which considers many variables is a powerful tool for optimizing the signal. The instability of the signal associated with the silica tube atomizer has also been solved with the factorial design. The methodology appears to be suitable for Sb determination in lubricating oils and can also be extended to Sn determination in canned edible oils and other types of fatty canned food.

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