FAAS Determination of Metals in Complex Paint Driers Using Microwave Sample Mineralization

***A. Lopez-Molinero, M.A. Cebrian, and J.R. Castillo**
Department of Analytical Chemistry, Science Faculty, University of Zaragoza, 5009 Zaragoza, Spain

ABSTRACT

A new, simple, and fast procedure is proposed for the determination of metals in complex soap paint driers. The method has been developed for multi-metallic driers; it has high potential throughput and can be applied to different metals. The procedure involves the complete decomposition and mineralization of the organic matrix of paint driers using acid attack with microwave heating and direct metal determination in aqueous solutions by flame atomic spectrometry in either the absorption or emission mode depending on the sensitivity of the elements.

Eleven elements (barium, calcium, cerium, cobalt, iron, lithium, manganese, lead, strontium, zinc, and zirconium) were determined in single-metal and multi-metal paint driers and the results are compared with standard or alternative procedures. The method is evaluated in terms of accuracy and uncertainty of the sample preparation and instrumental measurement steps.

INTRODUCTION

Paint driers are catalysts used in paint and varnish formulations to help accelerate the drying effects and the formation of films. They are considered the most important additives in the production of coatings in general (1).

High quality paint driers are principally metallic salts of octoic acids, ethyl-hexanoic, and other branched acids in which the metallic elements most frequently include Ba, Ca, Co, Mn, Pb, and Zn. Today, there is considerable interest in finding less contaminating metals with a faster drying effect. Many other metals (rare earth and transition metals) have been tested with alternative organic acids and are included in the paint drier compositions.

There is evidence that the technical performance and quality of these preparations depends to a considerable degree on the selected metal. In addition, cost is a major factor in the selection of the metallic content of metal soap driers. Both considerations are important in the evaluation of the metallic content of paint driers in the manufacturing practice.

From an analytical chemistry point of view, quality control of the production processes of frequently used paint driers, based on alkaline-earth or transition metals [as single-metal soap preparations with a typical metallic content of around 10% (w/w) or more], is usually performed by titrimetric or gravimetric methods which are used as reference methods (2-4). These methods are very suitable for specific metal determinations, even without isolation of the metals. However, their application to complex paint driers without previous metal isolation can be difficult and may cause interferences. In addition, standard methods based on direct dry ashing gravimetry are only suitable for high purity single-metal paint driers. Consequently, multi-metallic determinations in actual complex or mixed paint driers, involving other non-common metals, require validated instrumental methods.

There are not many published articles dealing with the metal determination in paint driers. However, the use of differential-pulse polarography (5,6) or flame atomic absorption spectrometry (FAAS) for the determination of Co and Pb in emulsified solutions (7) has been reported. These instrumental methods were selected due to their speed and simplicity, low matrix effects, and high throughput but were only applied to single-metal driers and showed a bias of around 2% to nominal values with a reproducibility around 2% RSD. These methods have their advantages but also show the need for better instrumental alternatives particularly for other non-common metals and complex multi-metal formulations.

A new and more general procedure is reported in the present paper which can be applied not only to common metals but also to more current formulations with non-common metals including refractory elements. The procedure is based on sample mineralization of the organic matrix using acid attack and heating in a microwave oven, which leads to a relatively simple matrix solution with a low salt content. Finally, the metallic content of aqueous solutions is determined by standard FAAS or flame atomic emission spectrometry (FAES) with practically no interferences. The analytical performance of this method is evaluated and the results compared with standard reference methods in terms of accuracy and reproducibility.

EXPERIMENTAL

Instrumentation

A PerkinElmer® Model 2380 flame atomic absorption spectrometer was used for all measurements (PerkinElmer Life and Analytical Sciences, Shelton, CT, USA). When the determinations were measured using flame atomic absorption spectrometry (FAAS), the instrument was equipped with PerkinElmer hollow-cathode lamps.

**Corresponding author.*
e-mail: anlopez@unizar.es

The standard nebulization system was used with burners for air-acetylene (10-cm slot) and nitrous oxide-acetylene (5-cm slot). The instrumental conditions for measuring the atomic absorption (FAAS) of Ca, Co, Fe, Li, Mn, Pb, Sr, Zn, and Zr, and the emission intensity (FAES) of Ba and Ce are given in Table I.

A microwave muffle furnace Model MAS 7000 (CEM, Matthews, NC, USA) for dry ashing was used with a magnetron of 1400 W at 2455 MHz.

A Multiwave® microwave digestion system (Anton Paar, Graz, Austria) was used for the microwave-assisted acid mineralization of the paint driers (mono- and multi-metallic driers). It was equipped with PFA vessels which can withstand a maximum operating pressure up to 75 bar and a maximum temperature of 220ºC. Since the pressure was monitored for all vessels, it was possible to maintain the maximum operating conditions during the entire digestion process and thus ensure complete digestion of the samples.

Two different operating conditions, referred to as Program I and II, were applied to the decomposition and are listed in Table II.

TABLE I
Instrumental Operating Conditions
for Flame Atomic Absorption or Emission Measurements

Element	Wavelength (nm)	Lamp Current (mA)	Flame	Technique	Working Range (µg mL^{-1})
Ba	553.6		N_2O-C_2H_2 Red, reducing	AES	0–20.0
Ca	422.7	5	Air-C_2H_2 Blue, oxidizing	AAS	0–5.0
Ce	269.9		N_2O-C_2H_2 Red, reducing	AES	0–500.0
Co	240.7	10	Air-C_2H_2 Blue, oxidizing	AAS	0–3.5
Fe	248.3	16	Air-C_2H_2 Blue, oxidizing	AAS	0–5.0
Li	670.8	5	Air-C_2H_2 Blue, oxidizing	AAS	0–3.0
Mn	279.5	7	Air-C_2H_2 Blue, oxidizing	AAS	0–2.0
Pb	283.3	5	Air-C_2H_2 Blue, oxidizing	AAS	0–20.0
Sr	460.7	15	N_2O-C_2H_2 Red, reducing	AAS	0–5.0
Zn	213.9	5	Air-C_2H_2 Blue, oxidizing	AAS	0–1.0
Zr	360.1	20	N_2O-C_2H_2 Red, reducing	AAS	0–600.0

TABLE II
Microwave Programs Used in the Mineralization of Paint Driers

Step	Initial Power (W)	Time (min)	Final Power (W)	Fan Speed (a.u.)
Program I				
1	100	5	600	1
2	600	5	600	1
3	1000	10	1000	1
4	0	15	0	3
Program II				
1	100	5	600	1
2	600	10	600	1
3	1000	15	1000	1
4	0	20	0	3

Reagents

Metallic standard stock solutions of 1000 mg L^{-1} were prepared for each element (Ba, Ca, Ce, Co, Fe, Li, Mn, Pb, Sr, Zn, and Zr) following the standard recommended procedures (8).

Additional dilute standard calibration solutions were prepared from the previous standard stock solutions immediately prior to use. In order to eliminate interferences (ionization, chemical), all metallic standard calibration solutions were prepared with 1% (v/v) HNO_3 to match the acid media of the sample mineralization procedure.

Other specific conditions considered for calibration or sample solutions containing certain metals were as follows: Barium solutions were made of 0.1% (w/v) potassium (as chloride), calcium solutions of 0.1% potassium and 0.1% Sr (as nitrate), cerium calibration standard solutions of 0.1% K, strontium solutions of 0.1% K, and zirconium solutions of 2125 mg L^{-1} Al and 0.4% (v/v) HF.

Deionized water of 18.2 MΩ.cm purity was obtained from a Milli-Q™ water system (Millipore, Bedford, MA, USA). Concentrated nitric acid [65% (w/w)] and all other chemicals used (Merck, Darmstadt, Germany; Fluka, Buchs, Switzerland and Aldrich, Milwaukee, WI, USA) were of P.A. grade.

Sample Preparation

The amount of the viscous driers ranged from 0.1 to 0.5 g according to their metallic content. In a typical case, 0.2 g of the paint drier was accurately weighed into PFA microwave digestion vessels and 5 mL of concentrated HNO_3 was added. The vessels were closed and placed into the microwave oven. Each sample was digested and analyzed with five replicates. After digestion and cooling, the attack solution was quantitatively transferred to 100-mL calibrated flasks and diluted to volume with deionized water.

Standard Reference Methods for Single-element Driers

Calcium

The sample (50–60 mg Ca) was dissolved with 10 mL of toluene, diluted with 2 mL of 2-propanol, and 3 mL of 4M HCl solution was added. Then, 10 mL of buffer solution (pH 10) was added to the solution and the mixture titrated using eriochrome black T. The color change was from violet-red to blue.

Cobalt

The sample (100–120 mg Co) was heated with 25 mL of 1M HCl, dissolved with 100 mL of 2-propanol. Then 15 mL of 40% hexamethylenetetramine was added and the mixture titrated using xylenol orange indictor. The color change was from violet to yellow.

Manganese

The sample (70–80 mg Mn) was dissolved in 10 mL of toluene and diluted with 50 mL of 2-propanol. Then about 0.1 g of ascorbic acid and 10 mL buffer solution (pH 10) was added and the mixture titrated with eriochrome black T. The color change was from violet-red to blue.

Lead

The sample (300–350 mg Pb) was dissolved in 10 mL of toluene and then diluted with 50 mL of 2-propanol. Then, 5 mL of 4M acetic acid (a few mg of tartaric acid can alternatively be used) and 25 mL of 0.1M EDTA were added. The EDTA excess was back-titrated with standard 0.05M Zn(II) (zinc sulphate) solution using eriochrome black T. The color change was from blue to violet-red.

Zinc

The sample (80–100 mg Zn) was dissolved in 10 mL of toluene and diluted with 50 mL of 2-propanol. Then, 10 mL of buffer solution (pH 10) was added and the mixture titrated using eriochrome black T. The color change was from violet-red to blue.

Zirconium

The sample (110–120 mg Zr) was dissolved with 40 mL of 2M sulphuric acid solution and heated to boiling for 5 min. After cooling, 25 mL of 0.1M EDTA solution was added. The solution was heated to boiling for 3 min, cooled and neutralized with ammonium hydroxide solution, then 25 mL of 30% (w/v) NaAc solution and 50 mL of acetone were added. The mixture was back-titrated with Zn sulphate using dithizone. The color change was from blue-green to red.

Iron

The sample (140–150 mg Fe) was dissolved with 15 mL of toluene, then 15 mL of ethanol and 25 mL of 2M sulphuric acid were added. The sample solution was boiled for 15 min and allowed to cool. Then 0.2 g of $NaHCO_3$, one drop of 0.01M ferroin solution (as redox indicator), and a few mL of 0.1M Ce(IV) standard solution were added until the color of the solution changed from red to green-yellow; then 0.2 g of $NaHCO_3$ and 4 g of KI were added. The mixture was left standing for 15 min in darkness and then titrated with 0.1M standard sodium thiosulphate solution using starch as the indicator. The color change was the disappearance of the blue starch-iodine color.

Barium

The sample (125–150 mg Ba) was mixed with 10 mL of concentrated sulphuric acid and a few mL of 30% (v/v) hydrogen peroxide. The solution was heated and diluted with deionized water and boiled. It was allowed to stand overnight to precipitate barium sulphate. The precipitate was filtered, dried, and heated in a microwave muffle at 800ºC and finally weighed as sulphate.

Cerium and Strontium by Dry Ashing Gravimetry

The sample (about 2 g) was placed into a quartz crucible and heated on a standard hot plate for about 1 h to eliminate the volatile content. It was then heated in a microwave muffle at 1000ºC for 10 min. After cooling, the ashes were weighed as oxides.

Lithium by Sulphate Dry Ashing Gravimetry

The sample (about 2 g) was placed into a quartz crucible with 2 mL of concentrated sulphuric acid, then heated on a standard hot

plate for about 1 h to eliminate the volatile content. Subsequently, the sample was heated in a microwave muffle at 1000ºC for 10 min. After cooling, the ashes were weighed as sulphates.

RESULTS AND DISCUSSION

Optimization of the Microwave Mineralization Program

A considerable number of articles deals with sample mineralization and preparation using microwaves. Generic and fundamental reviews can be found in the literature (9) as well as current trends and specific applications, i.e., for the determination of lead in paints related to driers (10–12).

In this work, three microwave digestion programs were tested to determine the one most suitable for the decomposition of organic driers. The microwave heating programs, the amount and type of acid as well as sample size used were initially in accordance with the manufacturer's recommendations (13).

Microwave programs I or II (listed in Table II) were applied to the digestion of reference drier samples and 5 mL of concentrated nitric acid was always used for the acid attack; flame atomic absorption spectrometry with air-acetylene flame (FAAS-Air) and nitrous oxide-acetylene (FAAS-NOX) or flame atomic emission spectrometry with nitrous oxide-acetylene flame (FAES-NOX) were used for the measurements. Single-metal driers containing Pb, Mn, Ce, and Zr were previously standardized by titrimetric or gravimetric methods. The results of the metal determinations are listed in Table III.

As can be seen, the results for Pb and Mn using Program I are in good agreement with those obtained using the reference methods. However, when applied to driers containing Ce or Zr (refractory elements), these elements were partially dissolved and the results obtained did not coincide with the reference results. Consequently, longer heating times were tested using Progam II. It was found that the difference between Programs I and II was the length of time for step 2 (at 600 W) and step 3 (at 1000 W). Program I required a total of 35 min compared with 50 min for Program II.

TABLE III
Metal Content Found by Reference Methods and the Alternative F-AS Method Using Microwave Programs I and II Acid Decomposition

Microwave Program	Drier Sample-Element Determined	Metallic Content[a] (g Metal/100 g Sample)		Type of Flame Method	Difference Between Means
		Reference Method	Flame Method		
I	M36-Pb	36.25±0.05	36.17±0.26	FAAS-Air	0.08
I	M6-Mn	6.30±0.10	6.12±0.03	FAAS-Air	0.18
II	M10-Ce	10.00±0.10	9.39±0.10	FAES-NOX	0.61
II	M12-Zr	12.03±0.01	12.10±0.41	FAAS-NOX	–0.07

[a] Means values ± s.d. from five independent determinations.

It can be seen that the Zr content found by the reference method is similar to that of the proposed method. However, the difference between the two methods is higher for Ce because the results obtained using the dry ashing gravimetry method are used as reference.

A third program, using shorter heating times and also requiring a smaller amount of nitric acid than for Program I, was devised in order to test the dissolution of common driers with transition metals. It was found that the results were not quantitatively comparable with the standard results. Consequently, programs using less heating time and less nitric acid than suggested in Program I are not recommended.

Program I was designed for and applied to the majority of common metals (alkaline earth and transition metals), whereas Program II was intended for refractory metals. Both programs are fast and reliable mineralization procedures that reduce the matrix content in the final sample solution and favor the implementation of instrumental measurements using simplified calibration.

Metal Determinations by Atomic Absorption or Atomic Emission and Influence of the Type of Flame

The performance of metal determinations (barium, calcium, cerium, cobalt, iron, lithium, manganese, lead, strontium, zinc, and zirconium) by FAAS or FAES and the use of air or nitrous oxide-acetylene flame were assessed.

FAAS measurements were carried out for Ca, Co, Fe, Li, Mn, Pb, Sr, Zn, and Zr. However, Ba and Ce were excluded on account of their low sensitivity. Standard air-acetylene flames were used in the determination of Ca, Co, Fe, Li, Mn, Pb, Sr, and Zn and a nitrous-acetylene flame was used for Sr (for comparison) and for Zr.

The results found with FAAS using air-acetylene flame (FAAS-Air), after drier mineralization by microwave heating and using Program I, are listed in Table IV. They are in good agreement with those found by the reference method, although Sr and to a lesser extent Zn show differences.

In the case of Sr, the difference could be due to the use of the less suitable air-acetylene flame for this metal (it does not impede chemical interferences) and the reference value obtained by dry ashing gravimetry does not discriminate possible interferences in the samples.

The difference with Zn is also appreciable. This metal was determined under different instrumental conditions using chemical standards of different quality, but the discrepancy always remained the same. The value of the difference was consistent with the magnitude of both methods, i.e., titrimetry used sample and reagents in 6-fold excess or more when compared to the instrumental method. Consequently and because this element is a well-known contaminant, the discrepancy was attributed to contamination.

A nitrous oxide-acetylene flame was also applied in the determination of Sr and Zr. This hotter flame is recommended as an alternative because it reduces chemical interferences during flame atomization. Mineralization using Program I or II for Sr and Zr, respectively, was used for their corresponding driers. The results of these determinations are also listed in Table IV (FAAS-NOX).

As can be seen, the bias for the Sr determination using the hotter flame has been reduced when compared to the air-acetylene flame. Although a discrepancy between the methods exists, it is less significant than in the results obtained for the "air" flame.

The Zr determination is in complete agreement with the reference value.

Ba, Ce, Li, Sr, and Zr were also determined by FAES using the hotter nitrous oxide-acetylene flame, which reduces chemical interferences. The results obtained after mineralization of the driers using the corresponding microwave Program I or II are listed in Table IV (FAES-NOX).

TABLE IV
Metals Determination in Drier samples by FAAS or FAES With Air-Acetylene or Nitrous Oxide-Acetylene Flame in Comparison to Reference Methods

Drier - Sample Element Determined	Metallic Content [a] (g Metal / 100 g Sample)		Type of Flame Method	Differene Between Means
	Reference Method	Flame Method		
M4-Ca	4.05±0.01	4.11±0.09	FAAS-Air	–0.06
M12-Co	12.19±0.01	12.10±0.23	FAAS-Air	0.09
M6-Fe	5.53±0.04	5.57±0.13	FAAS-Air	–0.04
M2-Li	1.70±0.11	1.85±0.03	FAAS-Air	–0.15
M6-Mn	6.30±0.01	6.12±0.03	FAAS-Air	0.18
M36-Pb	36.25±0.05	36.17±0.26	FAAS-Air	0.08
M18-Sr	17.06±0.38	16.41±0.18	FAAS-Air	0.65
M6-Zn	5.97±0.01	5.66±0.38	FAAS-Air	0.31
M18-Sr	17.06±0.38	16.67±0.26	FAAS-NOX	0.39
M12-Zr	12.03±0.03	12.10±0.41	FAAS-NOX	–0.07
M12.5-Ba	12.45±0.06	12.60±0.12	FAES-NOX	–0.15
M10-Ce	9.26±0.40	9.39±0.10	FAES-NOX	–0.13
M2-Li	1.70±0.11	1.84±0.03	FAES-NOX	–0.14
M18-Sr	17.06±0.38	16.57±0.29	FAES-NOX	0.49
M12-Zr	12.03±0.03	11.58±0.20	FAES-NOX	0.45

[a] Means values ± s.d. from five independent determinations.

The results for Ba and Ce are in very good agreement with the reference values and their biases are around 0.1 g per 100 g of sample. Lithium shows a similar bias to that found by FAAS-Air with high reproducibility (Std. Dev. 0.03). However, Sr has a higher bias than the bias found by FAAS-NOX. The results found for Zr are similar to Sr. Thus, it can be concluded that the metal determination by FAES-NOX is an improvement for the Ba and Ce paint driers.

Comparison of the Proposed FAAS Method With Reference Values

The accuracy of the results obtained in the determination of 11 metals in single-metal paint driers using the optimum mineralization and measurement conditions as listed in Table V was evaluated by comparing the reference values of standard methods using the straight line regression method.

In the linear comparison using the least squares method, the reference values were assigned to the x-axis and the best results of the proposed method to the y-axis. Figure 1 shows the linear graph, where each point represents the analysis of the same element in the same sample by two methods. The adjusted straight line gives the slope m = 0.9955 with a standard

deviation of sm = 0.0064, an intercept b = 0.0088 with a standard deviation of sb = 0.0920 and a regression coefficient r = 0.9998. The standard deviation of residuals was s y/x = 0.57. From these results and using the t-value (t = 2.26) for P = 0.05 and 9 degrees of freedom (11 points), the confidence limits for the slope and intercept are m = 0.9955 ± 0.0145 and b = 0.0088 ± 0.2079, respectively. These values confirm that the slope and the intercept do not differ significantly at P = 0.05 from the ideal values of 1 and 0, respectively. It can therefore be concluded that there is no significant difference between the new values and the reference values.

The residuals of the regression line listed in Table V show two important tendencies. The results obtained by FAAS using Program I and the air-acetylene flame are in close agreement with the reference values. When using Program II, the biggest differences are for elements with reference values obtained by the generic dry ashing gravimetry method (referred to as G-ashing in Table V).

Uncertainty of the Proposed FAAS Method

Uncertainty was considered an important factor in the analysis of real paint driers for quality control purposes, expressed as the standard deviation (s.d.) and variance. In order to evaluate the uncertainty, different sub-samples were taken and repeatedly measured so that the two sources of influence could be separated. The first source included sampling and sample preparation. The second source included measurements and interpolation in the calibration graphs, i.e., the influence of the preparation mode and the influence of the instrumental measurements. The results were

TABLE V
Comparison of Two Analytical Methods (Reference and Flame Methods) for Metals in Paint Driers by Linear Regression.
Differences Between Methods According to the Residuals of the Regression Line.

Element	Micro-wave Program	Reference Method	Flame Method	Residuals
Ba	I	G-ISO	FAES: N_2O-C_2H_2	0.1966
Ca	I	T-ISO	FAAS: Air- C_2H_2	0.0692
Ce	II	G-D-Ashing	FAES: N_2O-C_2H_2	0.1624
Co	I	T-ISO	FAAS: Air-C_2H_2	–0.0445
Fe	I	T-ISO	FAAS: Air-C_2H_2	0.0558
Li	I	G-D-Ashing	FAAS: Air-C_2H_2	0.1488
Mn	I	T-ISO	FAAS: Air-C_2H_2	–0.1607
Pb	I	T-ISO	FAAS: Air-C_2H_2	0.0726
Sr	I	G-D-Ashing	FAAS: N_2O-C_2H_2	–0.3228
Zn	I	T-ISO	FAAS: Air-C_2H_2	–0.2922
Zr	II	T-ISO	FAAS: N_2O-C_2H_2	0.1148

[a] G-ISO: Gravimetry by ISO 4619; T-ISO: Titrimetry by ISO 4619, G-D-Ashing: Gravimetry by dry ashing.

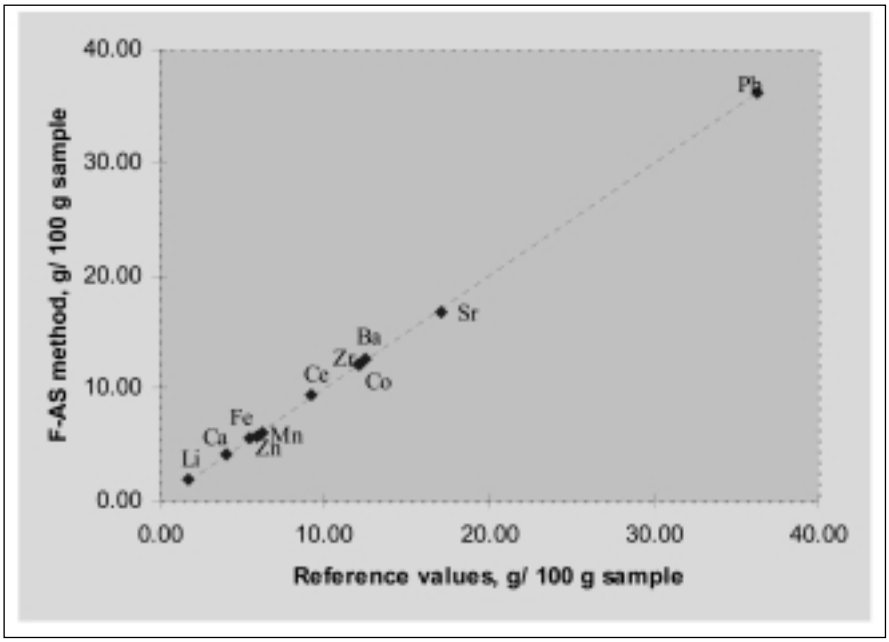

Fig. 1. Linear comparison of results by the proposed FAAS method with reference values of standard methods applied to the same elements in the same sample.

obtained by applying statistical ANOVA (14) and are listed in Table VI.

The results show that the total s.d. is affected mainly by the preparation step, whereas the measurement step is less significant for all of the metals.

The evaluation of the uncertainty ascribed to the individual steps shows that the sample preparation step has a s.d. of ≤0.1 g metal/100 g of sample for the majority of elements. Three elements have a s.d. of around 0.25, and only Zn and Zr display a value of around 0.4. The value for Zn is due to its contamination and the Zr value is due to its refractory behaviour. With regard to the uncertainty of the measurement step, it can be observed that all techniques show a low s.d. (s.d. of ≤0.1 g metal/100 g of sample) and this value is lower than 0.5 for the majority of the metals.

It should be noted that the sampling procedure is generally the major factor that influences the variance in the analysis. However, for these liquid samples, the homogeneity is good and, consequently, the variance of the first step (sampling and sample preparation) can be mainly identified with the variance in sample preparation.

TABLE VI
Uncertainty of Global Method, Preparation Step, and Measuring Step

Element-Flame Method	Standard Deviation		
	Total/(Metal Content) [a]	Preparation Step [b]	Measurement Step [c]
Ba-FAES: N_2O-C_2H_2	0.12/(12.60)	0.10	0.12
Ca-FAAS: Air- C_2H_2	0.09/(4.11)	0.09	0.02
Ce-FAES: N_2O-C_2H_2	0.10/(9.39)	0.10	0.03
Co-FAAS: Air-C_2H_2	0.23/(12.10)	0.23	0.04
Fe-FAAS: Air-C_2H_2	0.13/(5.57)	0.13	0.04
Li-FAAS: Air-C_2H_2	0.03/(1.84)	0.03	0.01
Mn-FAAS: Air-C_2H_2	0.03/(6.12)	0.025	0.015
Pb-FAAS: Air-C_2H_2	0.26/(36.17)	0.25	0.12
Sr-FAAS: N_2O-C_2H_2	0.26/(16.67)	0.25	0.09
Zn-FAAS: Air-C_2H_2	0.38/(5.66)	0.37	0.09
Zr-FAAS: N_2O-C_2H_2	0.41/(12.10)	0.41	0.04

[a] Total s.d. and metal content as g of metal per 100 g of sample.
[b] For 5 different sub-samples.
[c] For 3 replicates per sub-sample.

Multi-metal Determinations in Complex Driers

Since there were no certified reference multi-metal paint driers available and the reference method could not be applied to standard complex driers, the reliability of the proposed method was evaluated by analyzing real complex paint drier samples. The results obtained were compared with the alternative technique of inductively coupled plasma optical emission spectrometry (ICP-OES) using standard conditions (15).

The results obtained in the analysis of commercial paint driers containing nine metals (except for Ce and Fe which were not found in multi-metal commercial driers) using the proposed method with optimum microwave mineralization and flame atomic spectrometry are compared with the values obtained by ICP-OES (see Table VII).

The results are in good agreement for practically all of the metals, the differences being lower than 0.2 g metal/100 g of sample, except for Mn and Zr. A comparison of the means obtained with the two methods by linear regression showed that the confidence interval (at P = 0.05 and 7 degrees of freedom) for the slope was 0.9959 ± 0602, and the intercept was 0.1162 ± 0.3651. Consequently, both values include the reference data of 1 and 0, respectively. It can therefore be concluded that no systematic errors are introduced in the proposed method at the confidence level of P = 0.05.

CONCLUSION

The method proposed for the metals determination in single-metal and/or complex multi-metal paint driers is shown to be an alternative procedure to conventional methods and also overcomes some of their limitations.

The use of microwave digestion demonstrates that the samples were successfully mineralized (using 5 mL of nitric acid) with considerable speed, safety, and reduced sample preparation. The short Program I is recommended for Ba, Ca, Co, Fe, Li, Mn, Pb, Sr and Zn determination, while the long Program II is recommended for Ce and Zr determination. The metals Ca, Co, Fe, Li, Mn, Pb, and Zn were best measured by FAAS using air-acetylene flame; Sr and Zr by FAAS with nitrous oxide-acetylene flame; and Ba and Ce by FAES with nitrous oxide-acetylene flame.

TABLE VII
Determination of Metals in Complex Multi-metal Paint Driers by the Proposed Flame AS Method Compared with ICP-OES

Drier Metallic Composition	Determined Metal	Content by Flame AS[a]	Content by ICP-OES[a]	Difference of the Means
M 639-Ba,Co,Zn	Ba	7.45±0.12	7.60±0.23	–0.15
	Co	1.14±0.06	0.94±0.08	0.20
	Zn	3.70±0.03	3.86±0.06	–0.16
M 270-Ca,Co,Zr-	Zr	6.20±0.08	5.77±0.06	0.43
M745-Ca,Co,Li	Ca	4.23±0.20	4.31±0.01	–0.08
	Li	0.50±0.01	0.49±0.03	0.01
M 631-Ca,Co,Sr	Sr	4.43±0.09	4.38±0.09	0.05
M 26-Co,Mn	Mn	5.64±0.04	5.11±0.09	0.53
M 1012-Ca,Co,Pb	Pb	12.74±0.19	12.71±0.48	0.03

[a] Means of five independent determinations ± standard deviation; given as g metal/100 g sample.

The accuracy of the method shows a bias lower than 0.2 g/100 g of metal for the majority of metals, except for Sr and Zn. The uncertainty ascribed to the preparation step showed that it was the prevalent factor, whereas the flame atomic absorption spectrometric measurements always showed lower standard deviation values. This method can be adapted for other metals.

ACKNOWLEDGMENTS

The authors wish to thank Metalest (Zaragoza, Spain) for providing the paint drier samples and financial support.

Received July 3, 2003.

REFERENCES

1. J. Skalsky, Progress in Organic Coating 4, 137 (1976).
2. C.A. Luchesi and C.F. Hirn, Anal. Chem. 30, 1877 (1958).
3. International Organization for Standardization-ISO, Norm ISO 4619: Driers for paints and varnishes, Geneva, Switzerland (1998).
4. American Society for Testing and Materials-ASTM-, Standard D-564-47, Part 29, Vol. 20, p. 292, Philaphelphia, PA, USA (1980).
5. J. Garcia-Anton and J.L. Guiñon, Analyst 110, 1365 (1985).
6. J. Garcia-Anton and J.L. Guiñon, Analyst 111, 823 (1986).
7. J. Garcia-Anton and J.L. Guiñon, Analusius 14, 158 (1986).
8. Analytical methods for atomic absorption spectrophotometry. PerkinElmer Life and Analytical Instruments, Shelton, CT, USA (1982).
9. H.M. Kuss, Fresenius' J. Anal. Chem. 343, 788 (1992).
10. Microwave-enhanced chemistry. Fundamentals, sample preparation and applications. H.M. Kingston and S.H.J. Haswell, Eds.(American Chemical Society, Washington, D.C.,USA) (1997).
11. H.M.S. Kingston, At. Spectrosc. 19(2), 7 (1998).
12. D. Binstock, Anal.Lett. 33, 3397 (2000).
13. Microwave sample preparation system, Guide, Anton Paar GmbH, Graz, Austria (1998).
14. J.C. Miller and J. N. Miller, Statistics for analytical chemistry, Ellis Horwood, 2nd ed., New York (1988).
15. Plasma 40 Emission spectrometer, Guide, PerkinElmer Life and Analytical Instruments, Shelton, CT, USA (1987).