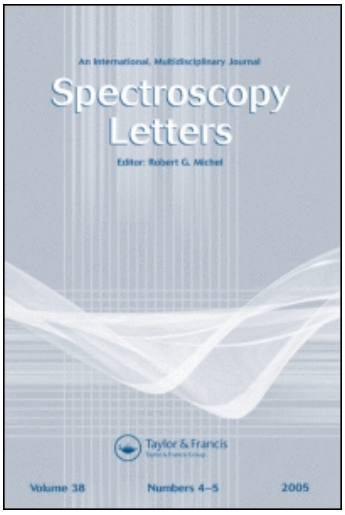

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Analytical Study of Raw Materials of Zinc Oxide Used for Enamels on Industrial Ceramics: Quantitative Analysis of Zinc, Lead, and Sulfur in These Samples by X-ray Fluorescence and Flame Atomic Absorption Spectrometry

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Analytical Study of Raw Materials of Zinc Oxide Used for Enamels on Industrial Ceramics: Quantitative Analysis of Zinc, Lead, and Sulfur in These Samples by X-ray Fluorescence and Flame Atomic Absorption Spectrometry

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Abstract: An analytical study is carried out to optimize X-ray fluorescence (XRF) and flame atomic absorption spectrometry (FAAS) quantitative analysis of Zn, Pb, and S in ZnO samples commonly used to obtain industrial ceramic enamels. Pb and S in the raw materials often contaminate ZnO and are very detrimental in industrial applications. Thus, very accurate analytical determination of these elements in ceramic samples is extremely important. First of all, a mineralogical study by X-ray diffraction (XRD) on the different components in these raw materials and the materials produced during the firing process is performed in order to establish the mineral forms in a reference sample for analysis by XRF spectrometry. The working conditions are optimized for XRF multi-elemental analysis, using the sample in the form of pellets, due to high loss on ignition (LOI) values. The preparation of suitable standards and working conditions for FAAS analysis have also been optimized. The content of these elements was determined by FAAS for the reference sample and several samples for industrial use, and the results were compared with those obtained by XRF. Comparison of the results obtained from

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XRF and FAAS analysis of Pb and Zn show more accurate values for FAAS. For ZnO, an accuracy of 0.11% with $\pm 0.1\%$ precision by FAAS and 0.46% accuracy with $\pm 0.2\%$ precision by XRF are found. For PbO, 1.06% accuracy and $\pm 0.06\%$ precision using FAAS and 5.6% accuracy and $\pm 0.35\%$ precision by XRF were found. For SO_3 determined only by XRF, accuracy was 4.76% with $\pm 0.25\%$ precision. These values are highly satisfactory given that these two elements are only found in small proportions.

Keywords: Ceramics, enamels, FAAS, lead, sulfur, XRD, XRF, zinc oxide

INTRODUCTION

Zinc oxide is widely used in the ceramics industry because of its significant influence on the development of synthesis methods[1,2] facilitating crystal growth,[3] improving dielectric properties[4] and the superconductivity of advanced materials.[5] It is a powerful, significant melt,[6] used especially for high-temperature enamels. It can also be used for low-temperature enamels, but in small percentages, because if too much is used, it stops acting as a melt and instead serves to increase the firing temperature. It also favors opacification when accompanied by other suitable basic oxides. Nowadays, zinc is used instead of tin (very expensive) to obtain white glass, although its use has been identified in 17th century enamels dated by X-ray fluorescence (XRF) and scanning electron microscopy–energy dispersive X-ray spectrometry (SEM-EDX) analysis.[7] It is also widely used in dental ceramics providing different shades of white for caps and anticarcinogenic dental formulation.[8] Zinc oxide has many applications in other fields,[9] as for example, in the manufacture of rubber fabrics,[10] papyrography,[11] catalysts,[12] fire-resistant materials,[13] and so forth. But it is used above all in paint manufacture because being an active basic pigment, it reacts with the binder and facilitates the mix and ground, controls consistency and penetration, improving the drying and hardening qualities of the film. In medicine, it is also used in ointments[14] applied externally to wounds, acting as a drying agent to limit secretions.

The main problem that occurs when using ZnO is the presence of PbO and SO_3 as contaminants. Pb and S are elements that are generally found in the presence of ZnO either in the raw materials used to obtain ZnO or during the firing process with very prejudicial effects for industrial applications, especially in relation to coloration. It is therefore of great interest to study their occurrence and quantify them accurately.

In this study, the elements present in several samples used in the ceramics industry were quantitatively analyzed by X-ray fluorescence (XRF) and flame atomic absorption spectrometry (FAAS), establishing a working procedure to optimize analysis of Zn, Pb, and S in samples of ZnO. The mineral form in which these elements occur in the unknowns was determined by X-ray diffraction (XRD). A reference sample of the main elements found was then obtained from analytical-grade chemical compounds. Calibration curves were also prepared with the elements in the form of the compounds found by XRD

analysis. In XRF spectrometry, the ideal quantification conditions were optimized for Zn, Pb, and S, including apparatus conditions, the range of concentrations of the calibration curves for accurate determination and the mineralogical influence of the standards, and so forth.

Similarly, for FAAS, calibration curves were obtained optimizing working conditions, but in this case, only for Pb and Zn analysis as this technique cannot be used to analyze S.

Finally, the proposed procedure to determine these elements in the ceramic samples by flame atomic absorption spectrophotometry and X-ray fluorescence spectrometry is described.

MATERIALS AND METHODS

Apparatus and Reagents

Instrumentation

The following instruments were used:

Muffle furnace (GALLUR max T 1300°C with temperature ascent speed regulator, Valencia, Spain); hydraulic press (HERZOG max P 40 ton, Osnabrück, Germany); Wolfram carbide disk mill (Fritsch pulverisette 9, Idar-Oberstein, Germany); agate ball mill (Fritsch pulverisette 7); crucible (5% Au/Pt ZGS); pelleter (Pt/Rh 30-mm diameter); X-ray fluorescence spectrometer (Phillips PW 2400 with rhodium anticathode controlled by SuperQ/Quantitative software version 1.1, Eindhoven, Netherlands); X-ray diffractometer (Siemens D500 controlled by DIFFRAC/AT version 3 software, Munich, Germany) with DIFFRACplus Evaluation Package Release 2001 and Powder Diffraction File (PDF) Release 1999 Database, provided by International Centre for Diffraction Data (ICCD); atomic absorption spectrophotometer (PU 9100X, Phillips).

Reagents and Samples

All the reagents used were Merck analysis grade.

Several industrial samples of ZnO were used, denominated M1, M2, M3, and M4, which have been provided by Euromap S.A. (Paterna-Valencia, Spain).

Standards for XRF calibration curves were elements in the form of different proportions of sulfates, except for Zn where zinc oxide was used.

Procedure

XRF Chemical Analysis

Firstly, a quantitative and semiquantitative analysis was done on the sample components using XRF to determine the presence of impurities, in particular S and Pb.

XRF analysis of standards and the unknowns was done on samples in the form of pellets with a ratio of 6:4 sample/diluent, using mannitol as diluent-compactant. To prepare the calibrating pellets, the reference materials ZnO, $PbSO_4$, Fe $(NH_4)(SO_4)_2$ $6H_2O$, and $CdSO_4$ were used in appropriate proportions to obtain a calibration curve with an oxide content similar to that of the samples to be analyzed. The total mass of the pellets was about 10 g. The sample and the diluent were porphyrized and mixed in a wolfram carbide ring mill and a ball mill successively, prior to pellet formation, which took place in a hydraulic press at a pressure of 30 tons for 1 min. The unknowns were prepared in the same way. Instrumental conditions for the different elements are shown in Table 1.

FAAS Chemical Analysis

The standard products mentioned above were used to determine Zn and Pb. To prepare the reference sample, the chemical compounds were suitably mixed in quantities of 1 g. They were dissolved in HNO_3 and calibrated in 1 L of deionized water.

HNO_3 was used to solve the unknowns, taking 0.25 g of samples and diluting in 250 mL mark flask.

A second dilution of the samples was carried out by nitrofluorhydric disgregation, dissolving the residue in HNO_3 and then diluting as before to 250 mL.

Pb and Zn standards were obtained from a 1000 ppm dilution of lead and zinc with deionized water as diluent and the appropriate dilution of zinc and lead concentrations to obtain a range of concentrations suitable for the determinations to be done, using dilutions with distilled water and solutions of Zn and Pb in similar concentrations to those in the matrixes of the unknowns. In Zn analysis, given its high concentration, a prior dilution of the samples from 1 to 100 ppm was done using either water or Pb solution. The instrumental conditions for the different elements are shown in Table 2.

RESULTS AND DISCUSSION

XRF and XRD Analysis

XRF Qualitative Analysis of Samples

The most significant elements detected are reported in Table 3, which shows X-ray fluorescence intensity values. These results suggest that the majority elements present with Zn in the samples are S, Pb, Fe, and Cd, so these five elements were chosen for determination. It can be seen that of the samples studied, the greatest quantities of S and Pb are found in sample M3.

Table 1. Working conditions of the different elements by XRF

Element	Line	X-tal	Collimator	Detector	Tube filter	kV	mA	E (keV)
Cd	Cd K_α	LiF 200	150 μm	Scint.	Brass (150 μm)	60	50	23.274
Fe	Fe K_α	LiF 200	150 μm	Flow	None	60	50	6.407
Pb	Pb L_α	LiF 200	150 μm	Scint.	None	60	50	10.582
Zn	Zn K_β	LiF 200	150 μm	Scint.	Brass (150 μm)	50	40	9.596
S	S K_α	PE 002-C	550 μm	Flow	None	25	125	2.313
Al	Al K_α	PE 002-C	550 μm	Flow	None	24	125	1.497
Si	Si K_α	PE 002-C	550 μm	Flow	None	24	125	1.743
K	K K_α	LiF 200	150 μm	Flow	None	24	125	3.314
Ca	Ca K_α	LiF 200	150 μm	Flow	None	30	100	3.691
Mn	Mn K_α	LiF 200	150 μm	Flow	None	60	50	5.899
Cu	Cu K_α	LiF 200	150 μm	Scint.	None	60	50	8.056
Ag	Ag K_α	LiF 200	150 μm	Scint.	Brass (150 μm)	60	50	22.091
Sn	Sn K_α	LiF 200	150 μm	Scint.	None	60	50	25.379

Table 2. Instrument conditions for the elements Pb and Zn by FAAS

	Pb	Zn
Burner angle	0° and 52°[a]	90°
Flame	Air/C_2H_2 Ox. Blue	Air/C_2H_2 Ox. Blue
Band pass	0.5 nm[b]	0.5 nm
Air flow	3.31 L/min	3.31 L/min
Acetylene flow	0.83 L/min	0.92 L/min
Wavelength	217 nm	213.9 nm
Intensity	10 mA	10 mA

[a]To low and high concentrations of Pb, respectively.
[b]0.2 and 0.5 nm band-pass were used to the regression line of Pb, respectively.

Loss on Ignition of the Samples

A study of loss on ignition of the samples at 1000°C has been carried out essentially to determine whether the samples could been used in XRF in the form of glass disks, which are to be preferred because the matrix effect is minor, but which require the samples and melts to be subjected to high temperatures.

The loss on ignition (LOI) at 1000°C for each of the samples was 2.48% for M1, 3.15% for M2, 4.37% for M3, and 2.90% for M4.

These results show considerable loss in the samples, which can be explained by two different effects, firstly decomposition of the sulfates with volatilization of SO_3 and secondly the fact that ZnO, PbO, and CdO are volatile oxides at 1000°C and therefore would be partially lost at firing temperature. Therefore, loss on ignition values are such that the use of the samples in the form of glass disks is not advisable and would be aggravated by the problems of determining Pb and Zn in contact with elements such as Fe_2O_2, which are easily reducible.[15] For these reasons, the use of pellets is completely necessary, so the mineralogical composition has to be known.

XRD Analysis of the Samples

A mineralogical study of the compounds present in the samples is done, as this is a key factor of interference in XRF elemental determination of these compounds. The minerals in the samples were studied using the diffractograms obtained by XRD, with the aim of using the found compounds to make the pellets for the calibration curves.

The diffractogram for sample M3 is shown in Fig. 1. It can be seen that there is a majority presence of Zn in the form of zincite, syn-ZnO, and Pb in the form of anglesite, syn-$PbSO_4$.

Table 3. Qualitative analysis of the unknown samples by XRF

Sample	Element	E- (keV)	Line	I_f- (kcps)
M1	Cd	23.274	Cd K_α	6.798
	Sn	25.379	Sn K_α	44.741
	Ag	22.091	Ag K_α	2.512
	Si	1.743	Si K_α	0.574
	Ca	3.691	Ca K_α	0.558
	Mn	5.899	Mn K_α	0.213
	Fe	6.407	Fe K_α	13.106
	Pb	10.582	Pb L_α	52.952
	Zn	9.596	Zn $K\beta$	1284.220
	Cu	8.056	Cu K_α	0.346
	K	3.314	K K_α	2.186
	Al	1.497	Al K_α	0.681
	S	2.313	S K_α	15.812
M2	Cd	23.269	Cd K_α	17.528
	Sn	25.379	Sn K_α	—
	Ag	22.091	Ag K_α	—
	Si	1.743	Si K_α	0.361
	Ca	3.692	Ca K_α	0.119
	Mn	5.902	Mn K_α	—
	Fe	6.408	Fe K_α	1.393
	Pb	10.581	Pb L_α	17.324
	Zn	9.596	Zn $K\beta$	1411.160
	Cu	8.059	Cu K_α	4.651
	K	3.314	K K_α	0.888
	Al	1.500	Al K_α	0.694
	S	2.313	S K_α	23.755
M3	Cd	23.270	Cd K_α	23.178
	Sn	25.384	Sn K_α	5.644
	Ag	22.192	Ag K_α	2.477
	Si	1.743	Si K_α	—
	Ca	3.694	Ca K_α	0.321
	Mn	5.902	Mn K_α	0.209
	Fe	6.407	Fe K_α	6.864
	Pb	10.581	Pb L_α	182.862
	Zn	9.596	Zn $K\beta$	1113.049
	Cu	8.059	Cu K_α	2.260
	K	3.314	K K_α	1.283
	Al	1.501	Al K_α	0.723
	S	2.313	S K_α	37.827

(*continued*)

Table 3. Continued

Sample	Element	E- (keV)	Line	I_f- (kcps)
M4	Cd	23.271	Cd K_α	19.825
	Sn	25.379	Sn K_α	—
	Ag	22.091	Ag K_α	—
	Si	1.743	Si K_α	1.952
	Ca	3.690	Ca K_α	2.515
	Mn	5.900	Mn K_α	1.005
	Fe	6.406	Fe K_α	40.943
	Pb	10.581	Pb L_α	50.034
	Zn	9.596	Zn $K\beta$	1259.573
	Cu	8.060	Cu K_α	2.266
	K	3.315	K K_α	1.446
	Al	1.495	Al K_α	3.030
	S	2.313	S K_α	24.013

These mineralogical forms indicate that the unknown material is not a natural raw material but obtained from a blend (ZnS) or from slices of metallic zinc that underwent a firing process in furnace. Minority elements are found as oxides, sulfates, and other intermediate compounds with no significant peaks on the baseline.

With the aim of determining its behavior with temperature, the unknown sample underwent an ignition process at 1000°C as it happens in industrial practice. The diffractogram for this sample is shown in Fig. 2. There is an almost total extinction of $PbSO_4$, and the presence of intermediate compounds such as lead oxide sulfate ($Pb_3O_2SO_4$) and lead oxide sulfate ($Pb_5O_4SO_4/PbSO_4.4PbO$) and possibly others resulting from the combination of sulfates with parts of ZnO. All of this occors as a consequence of the decomposition of sulfates at the temperatures of the firing process, and to the reactions in solid state at high temperatures among the present material. In this process, there are losses of some S as SO_3 and some Pb, possibly sublimated, which justify the loss on ignition (LOI). The diffractogram (Fig. 2) shows that zincite, syn-ZnO remains alter the firing process.

XRF Quantitative Analysis of the Samples

The pellets obtained from mixtures of ZnO and Pb, Fe and Cd sulfates provided the corresponding calibration curves which in turn provided the composition of each of the samples. The confidence intervals for slope (a) and y-intercept (b) were calculated as ts_a and ts_b, where s_a and s_b are the standard deviations of slope and y-intercept, respectively, and

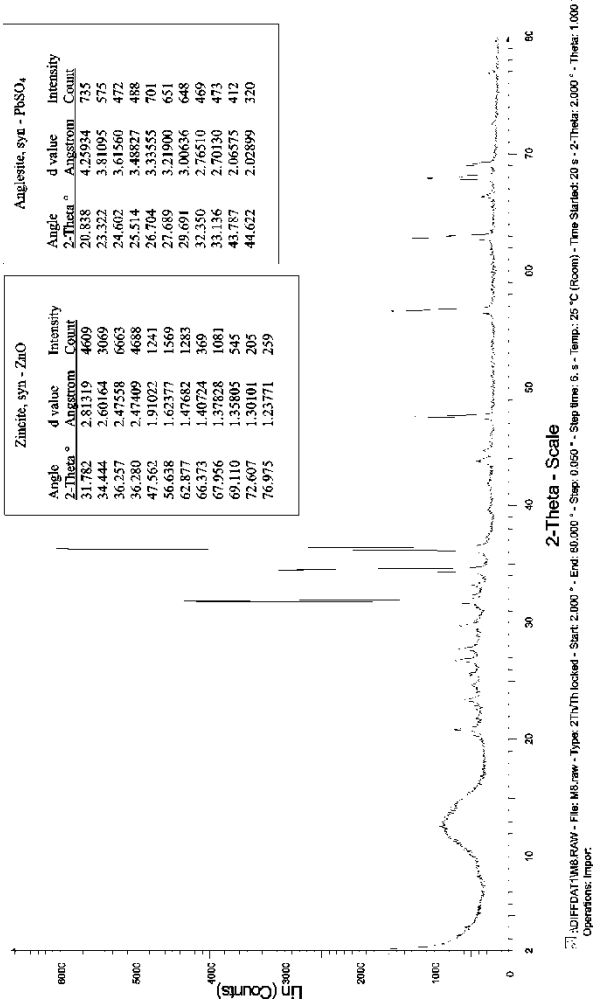

Figure 1. Diffractogram for sample M3.

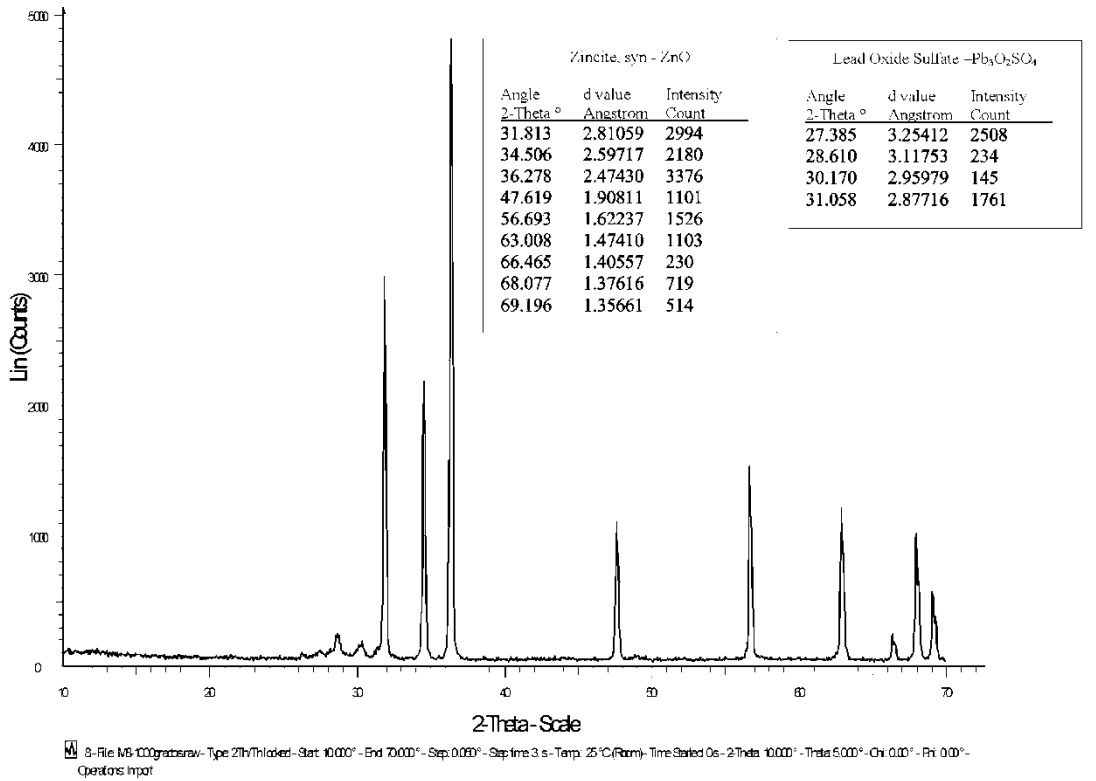

Figure 2. Diffractogram for sample M3 to 1000°C.

Table 4. Quantitative analysis of the unknown samples by XRF

% Oxides	M1	M2	M3	M4
ZnO	90.56 ± 0.33	96.83 ± 0.40	82.67 ± 0.25	89.81 ± 0.28
PbO	2.99 ± 0.20	0.96 ± 0.12	9.59 ± 0.35	2.78 ± 0.15
Fe_2O_3	0.44 ± 0.09	0.03 ± 0.01	0.22 ± 0.02	1.42 ± 0.10
CdO	0.19 ± 0.02	0.46 ± 0.05	0.75 ± 0.06	0.64 ± 0.06
SO_3	1.82 ± 0.24	2.80 ± 0.30	5.26 ± 0.33	3.07 ± 0.29
Others	4.00 ± 0.10	0.11 ± 0.01	1.51 ± 0.05	2.28 ± 0.07
LOI (1000°C)	2.48 ± 0.08	3.15 ± 0.10	4.37 ± 0.12	2.90 ± 0.09

n = 3.

t the Student's t (p = 0.05, gf = n − 1 = 2). The limit of detection was calculated as $3s_b/a$.[16]

The calibration curve obtained for SO_3 follows the equation: $y = (2.81 \pm 0.12)\ x - (0.4 \pm 0.7)$, with a correlation coefficient of 0.9998. The LOD found was 0.35 ppm.

ZnO, PbO, SO_3, CdO, and Fe_2O_3 contents were obtained from the corresponding calibration curves. The results obtained for the elements analyzed in the different samples together with loss on ignition values at 1000°C are shown in Table 4.

FAAS Analysis

In FAAS analysis, and given that the analytes are found in a type of compound (mineralogical form) that does not, in principle, influence their determination, the experimental work focused on choosing apparatus conditions in relation to different Pb and Zn concentrations and on sample and standard preparation, and also the most appropriate diluent, either deionized water or Zn, and Pb dilutions to determine Pb and Zn, respectively, obtaining calibration curves that are studied to optimize the method used.

Prior to the analytical study of Pb, two band-pass values were tested, 0.2 and 0.5 nm. The 0.2 nm value showed less sensitivity at low concentrations, while for moderate and high concentrations of analyte, sensitivity of both values was comparable and so in all cases a band-pass of 0.5 nm was used.

In general, on dissolving the samples with nitric acid, small residues were observed, in greater quantity in sample M4, probably due to the presence of different proportions of insoluble compounds, such as silica compounds, undissolved lead sulfate, and so forth. These residues become negligible when the sample is subjected to nitric/fluorhydric disaggregation.

Calibration Curves

Calibration curves for Pb and Zn were obtained from different types of dilutions according to the solvent used, deionized water and/or Zn or Pb dilutions, at concentrations similar to those that could be found in the samples, in order to minimize mutual interferences. The statistical treatment applied is the same as explained before.[16]

Firstly, the calibration curves for Pb were obtained in a wide concentration range (0.5–100 ppm of Pb). The results using water as solvent show that the absorbance signals versos concentration for levels above 10 ppm approximately give nonlinear values, so two different calibration curves had to be obtained, one for low Pb concentrations (Table 5) and the other for high Pb concentrations (Table 5). The LOD found were 0.23 ppm and 2.3 ppm, respectively. The calibration curve for Pb when using a Zn solution as diluent has a much smaller quantification limit so a single calibration curve can be obtained, provided concentrations are not excessively low (5–100 ppm); a calibration curve was obtained and is shown in Table 5, with an LOD of 1.0 ppm. Table 5 shows a calibration curve for the interval 0–10 ppm of Pb; an LOD of 0.13 ppm was calculated.

The absorbance signals obtained for the determination of Zn show identical values in both solutions with deionized H_2O and Pb solutions, showing the null interference of the presence of this element. The calibration curve of Zn is shown in Table 5, with a corresponding LOD of 0.07 ppm.

The results obtained for Pb and Zn analyzed in the different industrial samples are shown in Table 6. The table shows the data obtained from the samples subjected to a simple nitric dilution and that obtained by nitrofluorhydric disaggregation and subsequent dilution.

The results in Table 6 show slightly higher concentrations of analytes in the samples subjected to nitric/fluorhydric disaggregation, which indicates

Table 5. Statistical parameters of calibration curves for the elements Pb and Zn by FAAS

Element (concentration range, ppm)	Solvent	Burner angle	Regression line, $y = ax + b$; R^2				
			a	$\pm ts_a$	b	$\pm ts_b$	R^2
Pb (0–12)	H_2O	0°	8.42	0.25	−2.42	1.15	0.9993
Pb (0–120)	H_2O	52°	1.72	0.06	−0.4	2.0	0.9996
Pb (0–12)	Zn solution[a]	0°	10.05	0.18	−0.25	1.0	0.9999
Pb (0–120)	Zn solution[a]	52°	1.73	0.03	1.2	1.3	0.9998
Zn (0–12)	Pb solution[b]	90°	21.19	0.20	1.0	1.2	0.9999

[a]ZnO, 800 ppm.
[b]$PbSO_4$, 50 ppm.
n = 10.

Table 6. Determination of PbO and ZnO of the unknown samples by FAAS

	% Oxides	
	ZnO	PbO
M1		
HNO_3	89.10 ± 0.11	2.90 ± 0.02
HF	90.16 ± 0.12	2.90 ± 0.02
M2		
HNO_3	95.56 ± 0.17	0.86 ± 0.01
HF	96.08 ± 0.15	0.95 ± 0.01
M3		
HNO_3	81.89 ± 0.12	9.07 ± 0.07
HF	82.01 ± 0.10	9.19 ± 0.06
M4		
HNO_3	87.52 ± 0.12	2.48 ± 0.03
HF	89.02 ± 0.11	2.71 ± 0.02

n = 3.

that a small part of the sample did not completely dissolve after direct treatment with HNO_3, in accordance with the above-mentioned observations.

In order to compare the results obtained by XRF and FAAS, a reference sample was prepared with the following composition expressed in the form of oxides; 83.30% ZnO, 7.50% PbO, 1% Fe_2O_3, 1.80% SO_3, 1% CdO from ZnO, $PbSO_4$, $Fe(NH_4)(SO_4)_2$ $6H_2O$, and $CdSO_4$.

With these concentrations, six samples were prepared to determine the accuracy of the methods. The results obtained are shown in Table 7.

Comparison of the results obtained in the determination of Pb and Zn by XRF and FAAS show more accurate, precise results using FAAS, as can be seen from comparison of the methods with the synthetic reference samples, and although this means more laborious sample preparation, it has the advantage of being a technique that is independent of the mineral form of the analytes. However, the data obtained by XRF, for the reference sample and

Table 7. Determination of ZnO and PbO in the reference sample by FAAS and XRF

	Theoretical	FAAS	XRF
ZnO	83.30	83.39 ± 0.10	83.68 ± 0.20
PbO	7.50	7.42 ± 0.06	7.92 ± 0.35
SO_3	1.80	—	1.88 ± 0.25

the materials studied, are sufficiently acceptable for the technique to be an effective alternative; it can be applied using a less laborious technique and is necessary to determine SO_3 content as FAAS cannot be used in this case.

CONCLUSIONS

The qualitative study by XRF shows the presence of various impurities of different elements in different proportions, especially Pb and S, in the ZnO samples.

The X-ray diffractograms show that Zn as a majority element is found in the form of ZnO. Pb and other impurities are usually found in the form of synthetic sulfates. This indicates that they are products obtained from raw materials, blends (ZnS), or metallic zinc, subjected to heating in less than ideal conditions and lower temperature than 1000°C. If these samples were to be used for the incorporation of ZnO to enamels, they most likely would produce undesirable effects mainly in coloration, but also in other properties, depending upon the percentage of impurities, due to the presence of PbO and SO_3 within themselves and the possible contamination from sublimated Pb.

It can be deducted, from the values of loss on ignition and the diffractogram on the unknown material at 1000°C, that the determination by XRF of the standards and problem samples should be done in the form of pellets. Random losses of elements in the samples at high temperatures make it impossible to use glass disks.

The FAAS calibration curves suggest that lower quantification limits are needed to determine Pb when using standards in the presence of ZnO. For low concentrations (up to 10 ppm), the signals given using water as diluent are lower than those obtained using the ZnO matrix. For high concentrations, the absorbance signals for both matrixes are similar after 20 ppm, although the quantification limit is also lower when using ZnO as diluent, and at the same time a better regression coefficient is obtained. The best results are obtained with Pb concentrations of 5–100 ppm with ZnO matrix, which also offers the possibility of working with a greater range of concentrations.

The calibration curves for Zn determination show similar results using a Pb or water matrix, which shows that the presence of these elements does not influence Zn determination in the working conditions used.

The results are more precise when nitrofluorhydride disaggregation is used on the samples rather than diluted nitric acid. Therefore, in the analysis of this type of materials by FAAS, nitrofluorhydric disaggregation must be performed prior to dilution, because of the possible presence of insoluble residues, which, although in the samples studied are relatively unimportant, in others they may substantially modify the results obtained.

The results obtained for the analysis of Pb and Zn by FAAS are more accurate, and the process and technique used have greater precision. However, the results obtained using XRF are also acceptable, especially

from the viewpoint of the industrial use of these materials, which requires analytical information to be obtained quickly and reliably.

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