MULTI-ELEMENT ANALYSIS OF LUBRICATING OIL BY WDXRF TECHNIQUE

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ABSTRACT

The quantitative analysis of the chemical elements in matrices like oils or gels represents a challenge for analytical chemists. The classical methods and instrumental techniques such as atomic absorption (AAS) and plasma optical emission spectrometries (ICP-OES) need chemical treatments, mainly sample dissolution and degradation processes. X-ray fluorescence technique allows a direct and multi-element analysis with a simple sample preparation.

In this work, a sensitive method for Na, Mg, Al, Si, P, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Mo, Ag, Cd, Sn, Ba and Pb determination in lubricating oil using the WDXRF system is presented. The fundamental parameters method (FP) was applied and the sensitivity value for each element was determined by its calibration curve obtained from standard reference materials. The samples were prepared on a hot plate (60 ± 1C) into a platinum mould (50 ml). 1g of the sample was melted into 2g of the micro powder wax, obtaining a 25mm diameter and 10mm thickness merged disc.

The methodology validation (repeatability and accuracy) was obtained by analysis of the standard reference material SRM 1085b (multi-element standards S-21 from CONOSTAN®). The reference material data presented a precision, as relative standard deviation, between 1 – 5 % for all the elements, except for Ti and V determination (6.2 and 6.7 %, respectively). The accuracy of the method presented Z-score values between -2<Z<+2 for Na, Si, P, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Mo, Ag, Cd, Sn and Ba elements, what is indicative of the methodology validation for determination of these elements in oil samples.

Key words: X-ray fluorescence, lubricating oil, metal determination, methodology validation

1 INTRODUCTION

The strong industrial and urban development has been leading to a large consumption of automotive and industrial lubricating oils for their activities. For examples, in Brazil, circa of 900 million liters of the used lubricating oil per year are generated and only 10% is recycled. In countries such as Germany, England and USA, the used oil management is one of the requirements for environmental protection. Usually, in these countries, the used oils have to be collected and sent to adequate plants for recycling and reuse. Therefore, the processes seeking recycling and reuse and new analytical methodologies for inorganic contamination evaluation in lubricating oils have gained an important gap into economic and environmental protection context.

The quantitative analysis of the chemical elements in matrices like oils or gels represents a challenge for analytical chemists. The classical methods and instrumental techniques such as atomic absorption (AAS) and plasma optical emission spectrometries (ICP-OES), a complex sample dissolution or degradation processes are indispensable for inorganic analysis. The X-ray fluorescence technique presents some advantages, once it allows direct multi-elemental analysis without previous chemical treatments and only a simple sample preparation is usually required [1].

In this work, a methodology for the determination of the Na, Mg, Al, Si, P, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Mo, Ag, Cd, Sn, Ba and Pb elements in lubricating oil samples by wavelength dispersion X-ray fluorescence technique (WDXRF) using Fundamental Parameters (PF) method is presented.

2. EXPERIMENTAL

2.1 Sample Preparation

The sample preparation was carried out through following the steps. Initially, a 50 ml Pt/Au mold was filled with 2.00000±0.00005g of wax (MERCK, wax C micro powder). Afterward, 1.00000±0.00005 of the standard reference material SRM 1085b – multi-element standard S-21 from Conostan was added. The mixture was heated in a hot plate at 60 ± 1C until melting; subsequently it was homogenized, cooled and took off from the mold, obtaining a 25 mm diameter and 10 mm thickness merged disc.

2.3 Instrumental Parameters Condition

The experiments were carried out using a WDXRF spectrometer (RIGAKU Co. model RIX 3000, which comprised the following primary devices: one 3 kW Rh X-ray tube, 6 positions sample, 8 positions for Al, Ti, Ni and Zr filters, 3 collimators, 8 crystal analyzers, 2 detectors (scintillation and flow-proportional counters). The parameters such as voltage, current, collimator, analyzing crystal, detector and fixed counting time for Na, Mg, Al, Si, P, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Mo, Ag, Cd, Sn, Ba and Pb characteristic emission line were selected. (TAB. 1).

TABLE 1 – Measurements condition to WDXRF spectrometer (RIGAKU Co., model RIX 3000)

Excitation: 50kV x 50mA

Element	*Spectrum*	*Collimator*	*Analyzing Crystal*	*Detector*	*Counting time (s) Peak*
Na	Kα	480μm	TAP	SFP	40
Mg	Kα	480μm	TAP	SFP	40
Al	Kα	480μm	PET (111)	SFP	40
Si	Kα	480μm	PET (111)	SFP	40
P	Kα	480μm	Ge (111)	SFP	40
Ca	Kα	480μm	Ge(111)	SFP	40
Ti	Kα	480μm	LiF (200)	SC	20
V	Kα	480μm	LiF (200)	SC	20
Cr	Kα	160μm	LiF (200)	SC	20
Mn	Kα	160μm	LiF (200)	SC	20
Fe	Kα	160μm	LiF (200)	SC	20
Ni	Kα	160μm	LiF (200)	SC	20
Cu	Kα	160μm	LiF (200)	SC	20
Zn	Kα	160μm	LiF (200)	SC	20
Mo	Kα	160μm	LiF (200)	SC	20
Ag	Kα	160μm	LiF (200)	SC	20
Sn	Kα	160μm	LiF (200)	SC	20
Ba	Lα	480μm	LiF (200)	SC	20
Pb	Lβ1	480μm	LiF (200)	SC	20

TAP: thallium phosphate - LiF: lithium fluorite - Ge: germanium
SC: scintillation detector –NaI/Tl - FPC: flow-proportional counter.

2.4 Fundamental Parameters Method (FP)

The Fundamental Parameters method [2, 3] allows calculating the chemical composition of an unknown sample without specific standards necessity like in classical methods. The algorithm relates the measured fluorescent intensity of the analyte line, obtained from specific instrumental measurements condition, with "theoretical" intensities calculated from nuclear physical constants involving the parameters such as mass absorption coefficient, enhancement and specific absorption, X-ray yield and photoelectric phenomena. The sensitivity for each chemical element could be determined through parameters *a* (intercept) and *b* (slope) of the calibration curve and sensitivity curve is obtained by the relation between "theoretical" and measured fluorescent intensities. The good sensitivity curve is obtained when the mathematical coefficients of PF algorithm are determined from adequate standard samples [4].

The standard certified materials SRM 1085b – multi-element standard S-21, with 100, 200 and 500 µg g^{-1} in metal concentration, were prepared according to the procedure described in 2.2 item. The calibration curve ($I = a + bc$, where I = corrected fluorescent intensity; a = intercept, b = slope, c = concentration) for Na, Mg, Al, Si, P, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Mo, Ag, Cd, Sn, Ba and Pb elements was obtained using the corrections related to Fundamental Parameters algorithm, a software installed at spectrometer. In TAB. 2, the *a*, *b*, R^2 (linear coefficient) and *LQ* (limit of quantification) values are presented.

The quantification limit was calculated using the Eq. 1

$$LQ = \frac{I + 10 * s}{a} \tag{1}$$

where

I = "blank" fluorescent intensity, obtained from merged disc without SRM 1085b (Conostan S-21);
s = standard deviation "blank";
a = calibration curve intercept.

TABELA 2 – Calibration curves constants (a, b, R^2) and limit of quantification (LQ)

Element	*a*	*b*	R^2	*LQ (µg g^{-1})*
Na	0.1036	0.0039	0.9989	*0.4*
Mg	0.1525	0.0066	0.9930	*0.1*
Al	0.2118	0.0006	09984	*0.2*
Si	0.1062	0.0196	0.9913	*0.2*
P	0.1701	0.0564	0.9996	*0.4*
Ca	0.1445	0.3015	0.9983	*2.5*
Ti	0.0263	0.0979	0.9998	*3.8*
V	0.0345	0.1436	0.9999	*4.3*
Cr	0.0488	0.1978	0.9999	*4.3*
Mn	0.0650	0.2269	0.9999	*3.8*
Fe	0.0794	0.5632	0.9997	*7.8*
Ni	0.1069	1.2867	0.9999	*13.5*
Cu	0.1124	1.5916	0.9999	*16.0*
Zn	0.1142	2.7437	0.9997	*26.6*
Mo	0.095	11.758	0.9986	*12.4*
Ag	0.0739	10.017	0.9999	*7.1*
Sn	0.0199	-0.0145	0.9880	*3.8*
Ba	0.0270	0.0816	0.9786	*3.1*
Pb	0.1083	-0.1894	0.9985	*5.7*

a = intercept; b =slope; R^2 =linear coefficient values

2.5 Validation of the methodology

The methodology was evaluated using SRM 1085b - multi-element standard S-21 from Conostan with 100 μg ml^{-1} Na, Mg, Al, Si, P, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Mo, Ag, Cd, Sn, Ba and Pb content. Three samples were prepared and six measurements for each element were carried out. The experimental fluorescent intensities were interpolated in the sensitivity curve for their determination. The following statistical tests were applied for repeatability evaluation [4, 5].
At first, the Chauvenet's test was applied for outliers detection, according to Eq. 2 [6]

$$\left| X_i - \overline{X} \right| \rangle k_n s \tag{2}$$

where

X_i = measured value$_i$;
$\bar{x}$ = average;
k_n = Chauvenet's coefficient;
s = standard deviation.

Afterward, uncertainty test was applied for precision evaluation, using the Eq. 3 [7]

$$U = \pm t_{n-1(\alpha/2)} * \frac{s}{\sqrt{n}} \tag{3}$$

where

n = repetitions number;

s = standard deviation;

$t_{n-1\ (\alpha/2)}$ = t-Student value.

Finally, for accuracy evaluation the Z-score test was applied according to Eq. 4 [8]

$$z = \frac{\bar{x}_{\text{det}} - x_{cert}}{\sqrt{\sigma^2_{\text{det}} + \sigma^2_{cert}}} \tag{4}$$

where

$\bar{x}_{\text{det}}$ = experimental average;
x_{cert} = certificate value;
σ^2_{det} = experimental standard deviation;
σ^2_{cert} = certificate standard deviation.

III. RESULTS AND DISCUSSION

In TAB. 5, the experimental and certified values (average and uncertainty) of the SRM 1085b - multi-element standard S-21 material are listed. In the same Table, the calculated relative standard deviation (RSD %) and relative error (RE %*)* are also presented.

The precision of the results evaluated by *RSD %* values, showed a good repeatability for Na, Mg, Al, Si, P, Cr, Mn, Fe, Ni, Cu, Zn, Mo, Ag, Cd, Sn, Ba and Pb determination (less than 5.0 %); exception was observed for Ti and V determination, which showed 6.2 and 6.7 RSD % values, respectively.

The results evaluated by *RE %* values, *e.g.* comparing the certified and determined values, showed a relative error less than 5.0 % (0.4 to 4.8 %) for all elements determination, these results revealing an adequate precision and accuracy of the method for multi-elemental analysis in oil samples.

TABLE 5 – Experimental, certificate, RSD % (relative standard deviation) and RE % (relative error) values for SRM 1085b-multi-element standard S-21

Element	Experimental	Uncertainty	Certificate	Uncertainty	RSD	RE
	μg ml^{-1}	U (±)	μg ml^{-1}	U (±)	%	%
Na	104.2	2.0	100.00	0.01	2.5	4.2
Mg	104.6	1.4	100.00	0.01	1.7	4.6
Al	103.5	1.3	100.00	0.01	1.6	3.5
Si	104.8	2.3	100.00	0.01	2.9	4.8
P	103.4	3.5	100.00	0.01	4.3	3.4
Ca	103.2	3.0	100.00	0.01	3.8	3.2
Pb	95.4	1.7	100.00	0,01	2.4	4.6
Ti	101.2	4.8	100,00	0.01	6.2	1.2
V	101.8	5.3	100.00	0.01	6.7	1.8
Cr	101.8	2.6	100.00	0.01	3.3	1.8
Mn	102.3	3.6	100.00	0.01	4.6	2.3
Fe	99.6	1.3	100.00	0.01	1.7	0.4
Ni	96.6	2.5	100.00	0.01	3.3	3.4
Cu	103.7	1.5	100.00	0.01	1.9	3.7
Zn	95.1	1.3	100.00	0.01	1.8	4.9
Mo	104.6	2.4	100.00	0.01	3.0	4.6
Ag	102.6	2.0	100.00	0.01	2.5	2.6
Cd	101.3	2.2	100.00	0.01	2.8	1.3
Sn	97.2	1.7	100.00	0.01	2.3	2.8
Ba	103.3	1.9	100.00	0.01	2.3	3.3
Pb	95.4	1.7	100.00	0.01	2.4	4.6

The accuracy of the method was also evaluated by Z-score test, recommended by EURACHEM/CITAC Guide 4715-92, which values are showed in FIG. 1. The Na, Si, P, Cr, Mn, Fe, Ni, Cu, Mo, Ag, Cd, Sn and Ba determination presented Z-score values between -2<Z<2 proving statistically the accuracy of the method, once these values are accepted as satisfactory. The Al, Mg, Pb and Zn determination presented 2.1, 2.5, -2.1 and -2.9 Z-score values, respectively; which are considered questionable and Z-score value > $|3.0|$ is considered unsatisfactory. Thus, better instrumental conditions should be established for Al, Mg, Pb and Zn determination.

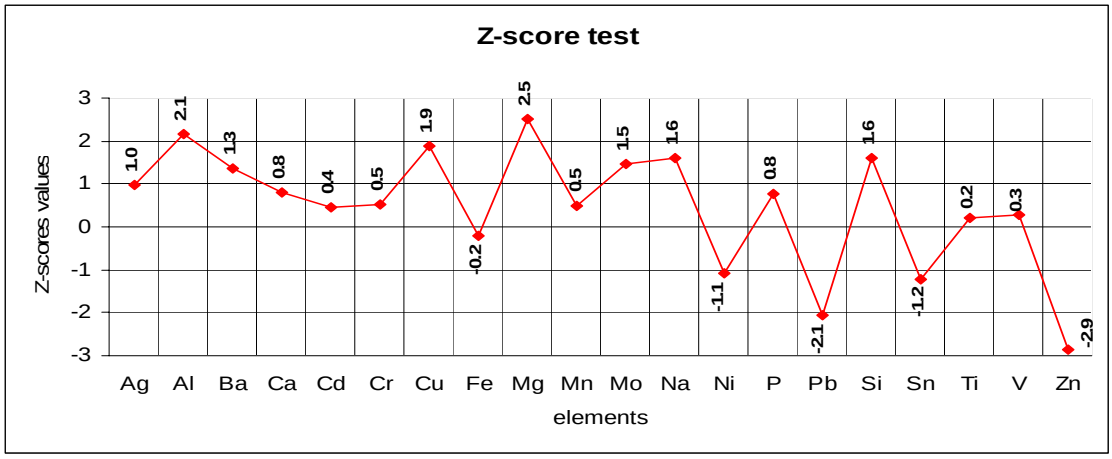

FIGURE 1 – Z-score values for Na, Mg, Al, Si, P, Cr, Mn, Fe, Ni, Cu, Zn, Mo, Ag, Cd, Sn, Ba nd Pb determination using the SRM 1085b – multi-element standard S-21 from Conostan

IV. CONCLUSION

The methodology allows Na, Si, P, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Mo, Ag, Cd, Sn and Ba determination in oleaginous materials with adequate precision and accuracy. The sample preparation is fast and easy and also has a low cost. The statistical tests applied in the SRM 1085b – multi-element standard S-21 from Conostan allowed the methodology validation.

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