

Determination of metals in lubricating oils by X-ray fluorescence spectrometry

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Abstract

The determination of common wear metals, namely iron, chromium, copper, zinc and lead, in a wide range of lubricating oil samples was investigated for the use of a low-cost, wavelength-dispersive X-ray fluorescence spectrometer. The procedure provided results in satisfactory agreement with inductively coupled plasma spectrometry used as reference method after microwave digestion of the samples in concentrated nitric acid. Statistical tests following extensive regression analyses of the data indicated that interelement effects were not statistically significant and that a simple linear regression was adequate for the calibration of individual metals. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The determination of metals and some other elements in lubricating oils has found wide application in industry, e.g. in the preventive care of mechanical failure of oil-wetted mechanisms (analysis of wear metals), in the control of various lubricant additives in finished oils, and for checking of toxic elements during liquidation of used oils.

A wide range of analytical procedures and methods for such determinations is described in

the literature. Flame atomic absorption spectrometry (FAAS) is one of the frequently used techniques [1–9], as concluded in a critical review [10]. However, this technique requires a prior treatment of oil samples which, in some cases, involves a complicated and time-consuming procedure. Solid particles above a critical size containing wear metals pass through the flame without undergoing complete decomposition and atomization; thus it is necessary to treat the oil samples with various mixtures of acids in order to dissolve the metal particles [1–3]. In the absence of such solid suspensions, it is possible to dilute the samples with a suitable organic solvent [4–6], e.g. xylene [7], to adjust the viscosity of samples. Mineralization by ashing [8,9] and formation of stable oils suspensions in water [10] are also used.

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The technique of electrothermal atomic absorption spectrometry (ETAAS) was recommended for the determination of 10 wear metals in aircraft lubricating oils after a dilution with kerosene. Precision of the method was found to be adequate in comparative studies of oil samples with metallic particles up to size of 20–30 μm [11].

Optical emission spectrometry with atomization in an inductively coupled plasma (ICP-OES) has also received considerable attention for the analysis of oils, also in comparison of measurements performed using FAAS. It was found to be of advantage for laboratories with large sample loads, as it offers simultaneous determination of many elements [10–15], greater linear working range, better freedom from chemical interferences and, in some cases, lower detection limits in comparison with FAAS [7]. Oils samples are only diluted with a solvent to adjust the viscosity [12–14]. Another recommended procedure involves leaching out the metals of an oil sample with hydrochloric acid with addition of hydrogen peroxide. The aqueous phase is then analysed with good agreement between ICP-OES and FAAS [15]. The introduction of oil samples into the ICP torch can also be realized with oil-in-water emulsions formed with addition of a surfactant [16]. A high temperature nebulization system with the use of Babington V-groove nebulizer and heated spray chamber allows to introduce a lubricating oil sample directly into the plasma torch [17]. Recently, electrothermal vapourization into inductively coupled plasma in combination with mass spectrometry was investigated for the determination of organo-metallic species in lubricating oils [18].

All the above-mentioned techniques have certain obvious disadvantages, i.e. beside expensive instrumentation (ICP-OES), they require high expertise for reliable operation and, in some cases, prior sample treatment (e.g. FAAS), which all contributes to the final price of analysis. X-ray fluorescence spectrometry represents a convenient alternative as it allows an easy and reliable measurement of well mixed oil samples without any additional sample treatment [19–21]. In the case of grease (e.g. a type of soap with graphite and varying oil content), for which it is difficult to

achieve reproducible filling of sample cups, simple mixing with a binder powder is recommended [22]. For X-ray fluorescence spectrometry, the calibration of the spectrometer represents the most challenging step of the analytical procedure: it should be realized that the results are not influenced by interelement effects, the light elements of the sample matrix or instrumental drift. The choice of a suitable set of calibrating standards is thus important. Commercially available single element standards (e.g. Conostan Metallo-Organic Standards [19]) were used to prepare synthetic standards in addition to some available standard reference materials (SRM; from the National Institute of Standards and Technology, Washington [20]). For the elimination of interelement effects, a large set of calibration standards is needed, which affects the cost of the analysis.

The present study was an investigation of the conditions to obtain a reliable determination of most common wear metals in lubricating oils with the use of a bench-top wavelength-dispersive X-ray fluorescence spectrometer of moderate price using oil standards with matrices identical with authentic oil samples.

2. Experimental

2.1. Instrumentation

For the determination of metals in reference samples of oils, which were then used for the calibration of the X-ray fluorescence spectrometer, an ICP spectrometer, type GBC Integra XL (GBS, Dandenong, Australia) was used. For all elements to be determined the following lines were selected in the first grating order: Fe 259.940 nm, Zn 213.856 nm, Cu 324.754 nm, Cr 283.563 nm, and Pb 227.353 nm. The technical parameters and settings of the spectrometer are listed in Table 1.

For the X-ray determination of metals in lubricating oil samples a bench-top, sequential, wavelength-dispersive spectrometer, type Spectroscan U (Spectron, St. Petersburg, Russia) was used, equipped with a bent lithium fluoride (200) crystal in a Johanson arrangement. A silver-target X-ray tube was operated at 40 kV (current 0.1 mA,

output 4 W). Measurements were performed in air. 2.5 ml sample was poured into a 30 mm diameter sample cup covered with a Mylar foil.

2.2. Reagents and materials

The calibration standards for the reference ICP-OES method were prepared from a multicomponent standard oil M 006 (Analytica, Prague, Czech Republic) with the following metal contents ($\mu\text{g g}^{-1}$): Pb 200; Al, Ti 100; Co, Ni, V, Zn 50; B, Fe, Cd, Cr, Cu 20; Mn 10; Ba, Se 5; and Be 2.

The applicability of the ICP-OES method was investigated with the use of synthetic oil blends based on single component standard oils, each one with a content of $1.000 \pm 0.005 \text{ mg g}^{-1}$ of Fe, Cr, Zn, Cu, and Pb, respectively, and a very pure base oil (Analytica).

For the decomposition of oil samples for the ICP-OES measurements, analytical grade concentrated (65%) HNO_3 was used.

For the calibration and X-ray fluorescence measurements, a series of oil blends was prepared from various used oils, namely, waste oil from a service station oil dump, oil from a vacuum pump and a hydraulic jack. For dilution of the mixtures, an unused oil, type Paramo R 825 (Paramo, Pardubice, Czech Republic) was used.

For dilution of decomposed samples, demineralized water was taken from a Milli-Q Plus water-purification system (Millipore, Bedford, MA).

Table 1

Technical parameters and settings of an optical emission spectrometer GBC Integra XL

Viewing height	7 mm
Monochromator grating groove density	1800 grooves mm^{-1}
RF generator power	1000 W
Argon flow in nebulizer	0.4 l min^{-1}
Pump revolutions	15 rpm
Photomultiplier voltage	600 V
Signal integration time	1 s
Number of replicate readings	3
Background correction	OFF peak

Table 2

Decomposition programme for oil samples with the use of a pressure digestion microwave apparatus Plazmatronika BM 1S/2

Step	Time (min) ^a	Output (%)	Reagent
1	5	70	HNO_3 concd.
2	7	80	—
3	10	90	—
4	15	100	—

^a Maximum total output of the microwave generator = 700 W; pressure = minimum 24 at; maximum 25 at.

2.3. Sample treatment

ICP-OES oil samples were first homogenized using ultrasonic mixing for 10 min. An amount of 300 mg of the sample was then weighed into a 150 ml polytetrafluoroethylene (PTFE) reaction vessel, 7 ml of concentrated HNO_3 (65%) was added and the sample was decomposed according to the programme given in Table 2 with the use of a pressure digestion microwave apparatus, type BM 1S/2 (Plazmatronika, Poznan, Poland). The obtained solution was then diluted with water to a final volume of 50 ml.

The calibration of the X-ray spectrometer was realized with the aid of authentic oil samples (mixtures of standard oils and also samples of used lubricating oils) which were chosen to form a calibration series for the contents of selected metals, i.e. Pb, Fe, Cr, Cu, and Zn, according to the results of ICP-OES. The applicability of the ICP method was verified, as described below, and found to be suitable as a reference method.

A series of standards was then chosen from the set of analysed oil samples to obtain concentration sequences of individual elements in order to represent mutually independent vectors allowing evaluation of the coefficients of interelemental effects involved in the calibrations.

Before each X-ray fluorescence measurement, an oil sample was mixed in an ultrasonic tank for 10 min and then introduced into the sample changer of the X-ray spectrometer. The same simple procedure was also used for the unknown oil samples.

Statistical calculations were realized with the use of a statistical PC program ADSTAT 2.0 (Trilobite Statistical Software, Pardubice, Czech Republic).

3. Results and discussion

3.1. Investigation of ICP spectrometry for reference assays of oil samples

A series of 11 oil standard samples containing all metals to be determined in the following ranges: 10–100 $\mu\text{g g}^{-1}$ for Cu and Cr, 10–500 $\mu\text{g g}^{-1}$ for Fe, and 10–2000 $\mu\text{g g}^{-1}$ for Zn and Pb, was prepared from single component oil standards by gravimetry. Each standard oil sample was then mineralized and the metal contents were determined by ICP-OES spectrometry.

The estimates of the regression line coefficients k_0 and k_1 were evaluated for each element by means of a program ADSTAT 2.0 as best fit for a regression line

$$C_{\text{ICP}} = k_0 + k_1 C_s \quad (1)$$

where C_s is an actual concentration of the metal and C_{ICP} is the metal concentration in $\mu\text{g g}^{-1}$ determined by ICP OES.

The Student's test was applied for the hypothesis $H_0: k_0 = 0$, or the alternative $H_A: k_0 \neq 0$. For the particular elements the tests (cf. ref. [23]) gave the following values: $t_{\text{Cu}} = 0.298$; $t_{\text{Cr}} = 1.375$; $t_{\text{Fe}} = 0.351$; $t_{\text{Zn}} = 1.971$; $t_{\text{Pb}} = 1.415$. As for the level of significance $\alpha = 0.05$ and two-sided testing, it was found that $|t| < t(0.975, 9) = 2.262$, the hypothesis that the regression line intercept was equal to zero was accepted for all of the above cases. Similarly, the test hypothesis $H_0: k_1 = 1$ against $H_A: k_1 \neq 1$ was found true for all elements as shown by the following values of the test criteria: $t_{\text{Cu}} = 0.258$; $t_{\text{Cr}} = -0.774$; $t_{\text{Fe}} = -0.480$; $t_{\text{Zn}} = -1.796$; $t_{\text{Pb}} = 0.226$; all of them were smaller than the critical t value. Thus, not a single case, the hypothesis of a unit slope value be rejected. As all regression lines passed through the origin and had slope values equal to unity, it was possible to conclude that the concentrations of particular elements found by the ICP-OES spec-

trometry showed no statistically significant difference from the theoretical values for all tested metals in the multielement oil standards. Therefore, the procedure of ICP-OES spectrometry was considered as successfully verified to be applied as the reference method.

3.2. Optimization of parameters for X-ray fluorescence analysis

For the X-ray assays, it was necessary to select a suitable analytical line together with the method of background correction. For the determination of Fe, Zn, Cu and Cr, K_α lines were used. For the determination of Pb L_α line was chosen. The position of a two-point background correction was chosen on the basis of scans of the particular analytical line in a real sample of used oil containing high amounts of all metals to be determined. The background intensity measured at the two chosen points should not be influenced either by the relevant analytical line or by a line of another element present in the sample. The selection of wavelengths of the individual analytical lines for the elements to be determined, $\lambda(K_\alpha)$ or $\lambda(L_\alpha)$, together with the positions of the points for the background correction, λ_1 and λ_2 , was as follows (in 10^{-3} Å): Fe $\lambda(K_\alpha) = 1937$, $\lambda_1 = 1870$ and $\lambda_2 = 1970$; Zn $\lambda(K_\alpha) = 1436.5$, $\lambda_1 = 1350$ and $\lambda_2 = 1480$; Pb $\lambda(L_\alpha) = 1176$, $\lambda_1 = 1120$ and $\lambda_2 = 1220$; Cu $\lambda(K_\alpha) = 1542$, $\lambda_1 = 1480$ and $\lambda_2 = 1630$, Cr: $\lambda(K_\alpha) = 2291$, $\lambda_1 = 2260$ and $\lambda_2 = 2320$.

For each element, the integration time of the signal used for the calibration was also optimized. A sample containing an average concentration of the metals to be determined was used for 10 subsequent measurements of the K_α line intensity for the chosen integration times (1, 10, 50, 100, and 200 s). Each obtained set of values, corrected for the background, was used to calculate a standard deviation typical for the particular signal level. Plots of these values, as function of the integration time, revealed that they were influenced by the signal intensity of the measured metal. If the intensity was higher than 5000 cps, it was possible to observe first a decrease of the standard deviation up to an integration time of 50 s and then, for the integration time higher than 50

s, there was an increase of the standard deviation. In Fig. 1, for example, such a dependence, as observed with Zn, is illustrated. When the signal intensity was lower than 3000 cps, the standard deviation decreased within the whole range of the integration times (1–200 s); this was the case of Fe (Fig. 1). For a group of metals (Cu, Pb, Zn), for which the sensitivity of the method was sufficient and the average content in the samples adequate to exceed the signal intensity level of 5000 cps, an integration time of 50 s was chosen; for the other elements, i.e. Fe and Cr, with signal intensities below a value of 3000 cps, an integration time of 100 s was chosen as a compromise.

3.3. Calibration of the X-ray fluorescence spectrometer

The calibration series consisted of 18 different samples of lubricating oils in which the metal content was determined by ICP-OES spectrometry as described above. The concentration ranges for particular elements in the oil samples were for Cu and Cr 10–100 $\mu\text{g g}^{-1}$, for Fe 10–500 $\mu\text{g g}^{-1}$, and Zn and Pb 10–2000 $\mu\text{g g}^{-1}$.

For these standard samples, the intensities of relevant analytical lines were corrected for the background intensity and were plotted against the metal content in the sample.

The signal intensity of the analysed element is generally influenced, besides its actual concentration, by the presence of some other elements in

the sample. The greatest effect is shown by elements with atomic numbers 1 and 2 lower or higher of then the measured element. These factors should be taken into consideration in the calibration procedure. In the software package supplied with the Spectroscan U spectrometer, the following regression equation is provided to correct for interelement effects.

$$C_1 = \beta_0 + \beta_1 I_1 + \beta_2 I_2 + \beta_3 I_1 I_2 + \beta_4 I_1^2 + \beta_5 I_2^2 \quad (2)$$

where C_1 denotes the sample content of the analysed metal in $\mu\text{g g}^{-1}$, I_1 the signal intensity of the analysed metal in cps and I_2 the line intensity of an interfering element in cps. In order to include these effects into the calibration of the X-ray spectrometer, the significance of relevant parameters was tested with the use of a statistical program ADSTAT 2.0 for the regression analysis of the model in Eq. (2). In the case of Fe, the intensity of a K_α line of Cr was substituted for I_2 , in the case of Cr it was the Fe K_α line, for Zn the interference of Cu was considered and vice versa. For a Pb L_α line, no interference of any metal present was considered and so the terms with I_2 were omitted in the tested regression model. So, all parameters with the terms referring to the interelemental effects were evaluated for the elements investigated, together with that of the square intensity I_1 of the metal to be determined. Student's test of the hypothesis $H_0: \beta_x = 0$ ($x = 2-5$) against $H_A: \beta_x \neq 0$ ($x = 2-5$) was used for all these individual parameters in the regression Eq. (2). For the parameters β_2 , β_3 , β_4 and β_5 , the calculated t values showed that for all cases the test zero hypothesis was true: $|t| < t(0.975, 12) = 2.179$; thus, all interference parameters in Eq. (2) could be considered as statistically insignificant.

It was possible, therefore, to test the calibrations in the form of the following simplified regression model

$$C_1 = \beta_0 + \beta_1 I_1. \quad (3)$$

Program ADSTAT 2.0 was also used to test the statistical significance of the relevant regressions for the two models. The F -test values for the significance of the particular regressions were compared with the corresponding critical values. In addition to that, further statistical characteris-

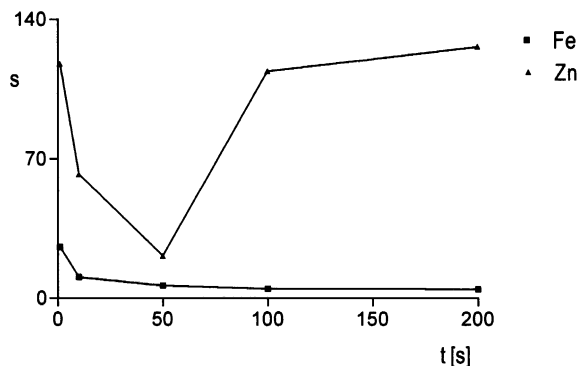


Fig. 1. A plot of the absolute standard deviation of the signal intensity for iron and zinc versus signal integration time.

Table 3

Comparison of statistical characteristics of a regression model with quadratic terms and the terms expressing interelement effects [Model 1, Eq. (2)] with a simplified linear regression [Model 2, Eq. (3)]

Metal	MEP		AIC	
	Model 1	Model 2	Model 1	Model 2
Fe	885	83.5	79.3	78.4
Cr	2.45	0.70	−0.89	−6.92
Cu	21.7	11.0	40.5	34.6
Zn	1607	373	97.0	89.3
Pb	556	28.3	34.3	31.6

tics, namely the mean square error of prediction (MEP) and Akaike information criterion (AIC) were evaluated (Table 3). For all elements to be determined, these characteristics were lower for the simplified regression model in comparison with that in Eq. (2).

Therefore, working calibrations of the X-ray spectrometer were based on the simplified regression model, as exemplified by the following equations (with 95% reliability intervals for the line intercept and slope value):

$$C_{Zn} = -3.58 \pm 9.57 + (0.458 \pm 0.00059)I_{Zn} \quad (S_{yx} = 18.4) \quad (4)$$

$$C_{Fe} = 6.98 \pm 3.69 + (0.154 \pm 0.0029)I_{Fe} \quad (S_{yx} = 8.38)$$

$$C_{Cr} = -0.15 \pm 0.25 + (0.666 \pm 0.012)I_{Cr} \quad (S_{yx} = 0.777)$$

$$C_{Pb} = -1.05 \pm 5.58 + (0.106 \pm 0.00086)I_{Pb} \quad (S_{yx} = 17.6)$$

$$C_{Cu} = -107.7 \pm .4 + (0.064 \pm 0.0013)I_{Cu} \quad (S_{yx} = 2.98).$$

In the case of copper, the calibration line did not pass through the origin. The non-zero values of the signal, when this metal was not present, were attributed to scattered radiation from a copper jacket of the X-ray tube.

3.4. Evaluation of the detection limit for individual metals

The detection limit (DL) was calculated as the concentration corresponding to a threefold standard deviation of the particular uncorrected analytical line at such metal content which was close to the determination limit, i.e. when the net intensity of the signal corresponded to 6–10-fold times standard deviation of the background intensity at the position of the particular line. Thus, the detection limit was based on 10 subsequently repeated measurements of a sample containing the metal content yielding the required intensity, with an integration time corresponding to that of the calibration measurements. The following values of the detection limits (DL) in $\mu\text{g g}^{-1}$ were thus obtained: $DL_{Fe} = 1.20$, $DL_{Zn} = 1.24$, $DL_{Pb} = 7.11$, $DL_{Cu} = 2.13$, $DL_{Cr} = 1.76$.

3.5. Accuracy of the X-ray spectrometry method with respect to ICP spectrometry in assays of lubricating oils

In ten samples of used mineral oils, the content of Fe, Cr, Zn, Cu, and Pb was determined using both X-ray spectrometry (XRF) and ICP spectrometry (ICP-OES), when in the latter case microwave digestion of samples concentrated HNO_3 was used. For individual metals the program AD-STAT 2.0 was again used to evaluate the parameters of the following regression equation

$$C_{XRF} = k_0 + k_1 C_{ICP} \quad (5)$$

where C_{XRF} represents the content of a particular metal in $\mu\text{g g}^{-1}$ found by X-ray spectrometry and C_{ICP} denotes the metal content in $\mu\text{g g}^{-1}$ determined by ICP-OES spectrometry.

A zero hypothesis, $H_0: k_0 = 0$, was then tested against the alternative hypothesis $H_A: k_0 \neq 0$ with the aid of the Student's test. For individual metals, the following t -values were evaluated (cf. [23]): $t_{Cu} = 0.041$; $t_{Cr} = -0.474$; $t_{Fe} = 1.051$; $t_{Zn} = 0.983$; $t_{Pb} = 1.065$. As for all these cases, the test values fulfilled the criterion $|t| < t(0.975, 8) = 2.306$, the hypothesis that the line intercept is equal to zero was considered to be true. For each metal the subsequent zero hypothesis $H_0: k_1 = 1$

Table 4

Results of determinations of selected metals in oil samples (in $\mu\text{g g}^{-1}$) using ICP spectrometry (ICP-OES) and X-ray spectrometry (XRF)

Sample	C_{Zn}		C_{Cu}		C_{Fe}		C_{Cr}		C_{Pb}	
	ICP	XRF	ICP	XRF	ICP	XRF	ICP	XRF	ICP	XRF
A	45.6	39.1	43.7	47.1	189.0	185.5	8.0	8.1	16.3	16.5
B	173.5	178.2	107.4	101.5	23.4	22.5	5.8	4.8	14.3	18.9
C	982.5	956.3	24.6	27.3	22.7	23.4	4.6	4.6	13.2	13.0
D	1196	1179	14.7	10.3	34.4	47.1	8.7	5.4	2155	2065
E	1056	1059	13.1	11.9	42.9	35.1	30.9	31.2	20.3	20.7
F	377.5	380.0	51.9	58.9	21.2	24.0	0.0	4.0	746	787
G	1087	1048	9.1	6.4	65.0	65.1	7.1	7.3	20.2	21.1
H	360	376	53.7	57.1	63.5	66.1	53.7	57.1	1198	1235
I	15.2	16.3	13.0	10.7	62.5	65.7	12.9	10.7	321	357
J	568	579	71.8	70.7	20.7	21.3	41.4	40.9	111	103

was then tested against the alternative $H_A \neq 1$ to yield the following t -values: $t_{\text{Cu}} = -0.104$; $t_{\text{Cr}} = 0.762$; $t_{\text{Fe}} = -0.883$; $t_{\text{Zn}} = -2.080$; $t_{\text{Pb}} = 1.559$. As in all tested cases when the calculated t -values were smaller than the critical value 2.306, the zero hypothesis that the slope value was equal to unity was found to be true.

Since for all metals, the regression lines (5) passed through the origin with unit slope values, it was possible to assume that there was no significant statistical significant difference between the results of the two tested methods. The results of assays of some ten real oil samples, which are listed in Table 4 for the two methods, allow comparison of the applicability of the proposed procedures in analytical practice.

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