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A multicommuted flow system for the determination of copper, chromium, iron and lead in lubricating oils with detection by flame AAS[☆]

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Abstract

In this work, a flow analysis procedure for the determination of copper, chromium, iron and lead in lubricating oils using flame AAS as detection technique is described. The flow manifold was designed to implement the multicommutation approach and it comprised three 3-way solenoid valves controlled by a personal computer. The flow system presented allowed to process the oil samples to determine wear metals without any prior preparation. Aiming to assess accuracy the results were compared with those obtained by manual procedure using flame AAS. Applying the joint-confidence ellipse test, no significant difference at the 95% confidence level was observed. Other profitable features such as a sample throughput of 50 determinations per hour; relative standard deviations ($n = 5$) below 2% for Cu, and below 8% for Cr, Fe and Pb; and linear responses in the range 0–40 ppm (w/w) (Cu, Fe) and 0–15 ppm (w/w) (Cr, Pb) were also achieved.

Keywords: Flow analysis; Multicommutation; Lubricating oil; Flame atomic absorption spectrometry; Copper, chromium, iron and lead

1. Introduction

A usual practice in engine maintenance is the determination of the contents of certain metals in the used lubricant oil [1,2]. This task is implemented as a part of predictive or proactive maintenance programmes of large engines such as those used in ships, aircraft, locomotives and trucks. This approach is different to classical preventive maintenance, where lubricating oil should be changed on a mileage basis. In predictive maintenance, the physicochemical properties of the oil are studied in order to determine the appropriate time to replace it. Besides, the inner wear of engines is monitored through the analysis of the contents of metals in the oil.

To attain this goal, detection techniques such as flame atomic absorption spectrometry (FAAS) [3], inductively coupled plasma optical emission spectrometry (ICP-OES) [3,4], X-ray fluorescence (XRF) [5] have been employed. Nevertheless, the high viscosity of the oil sample requires laborious handling to assure the robustness of the data. The sample manipulation can become a tedious task when a large amount of samples must be analysed considering that sample aliquot must be weighted and this step requires a careful manipulation. In this sense, a mechanised procedure simplifying the sample preparation step such as those based on flow analysis [6] should be appreciated.

The flow analysis techniques have been widely employed to develop analytical procedures involving aqueous matrices [7,8], solid samples [9,10], etc. Among the detection techniques in flow analysis, flame atomic absorption spectrometry has been widely employed for determination of metals [11–13]. Nevertheless, there is a scarcity of procedures based on flow analysis concerning to the determination of metals in lubricant oil samples [14,15].

Lubricating oil is a complex matrix [16] and an analytical procedure for the determination of wear metals without a prior treatment can be hindered by its high viscosity, thus requiring its previous dilution using a solvent [14] or the injection of the sample aliquot into a kerosene stream [15].

In this work, we intend to develop a multicommutated flow procedure for the determination of Cu, Cr, Fe and Pb

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in used lubricating oil employing flame atomic absorption spectrometry as detection technique. Aiming to the development of an analytical strategy to process oil samples without any prior preparation, the multicommutation flow process [17] was selected considering its well-known ability to handle solutions [18–20]. The main difficulty expected is related to the viscosity of sample, thus considering this feature the manifold is designed to mix the solvent fluid with the sample aliquot on line by means of a packed mixing reactor.

2. Experimental

2.1. Apparatus

The equipment set up was constituted by a Perkin-Elmer 380 atomic absorption spectrometer furnished with Photron (Narre Warren, Australia) hollow cathode lamps; a Rainin (Woburn, USA) Dynamax RP1 peristaltic pump furnished with Viton® pumping tubes; a Cole Parmer (Vernon Hills, USA) potentiometric strip-chart recorder; a 12 V regulated power supply source to drive the solenoid valves, and a lab-made electronic interface to control the solenoid valves through the personal computer LPT1 parallel printer port.

The spectrometer was operated with air–acetylene flame and a 10 cm burner, the wavelengths being 248.8 nm (Fe), 324.7 nm (Cu), 283.3 nm (Pb) and 357.9 nm (Cr). Other conditions were set up as recommended by the manufacturer.

The flow manifold was designed involving three 3-way solenoid valves (NResearch, West Caldwell, USA, type HP225T031), two PTFE joint devices (Omnifit, Cambridge, UK) a lab-made packed mixing reactor described elsewhere [15], a lab-made hydrostatic column (described below under Section 2.3) and flow lines made of Teflon PFA tubing (0.8 mm i.d.).

The packed mixing reactor consisted in a 10 cm long piece of PTFE tubing (inner diameter, 2.5 mm) filled with small pieces of the same material resulting in an empty volume of 350 μL. The purpose of this device was to allow a thorough radial mixing of sample and carrier solvent.

2.2. Standards, samples and reagents

CONOSTAN (Ponca City, USA) S-21 500 ppm multielemental standard solution was diluted as necessary with an oil mixture of BO-75 (CONOSTAN) and Superdiesel 40 (ANCAP, Montevideo, Uruguay). The amounts of BO-75 in the mixture were adjusted in each case to keep the viscosity at a constant level.

Samples of used Superdiesel 30 and 40 lubricating oils (ANCAP) were obtained from diesel engines of locomotives and ships. The service time of the samples spanned a range from 50 to 2000 h.

Deodorised kerosene (ANCAP), checked to be metal-free, was used as the solvent/carrier fluid.

2.3. Flow system

The flow manifold was designed to implement the multicommutation approach and to do this the solenoid valves were assembled as depicted in Fig. 1. In order to drive the oil samples, a piece of Tygon tubing (internal diameter 1.85 mm) was used to implement a vertical hydrostatic column (HC) with a height of 90 cm (measured from sample level to waste level) thus providing an appropriate driving force.

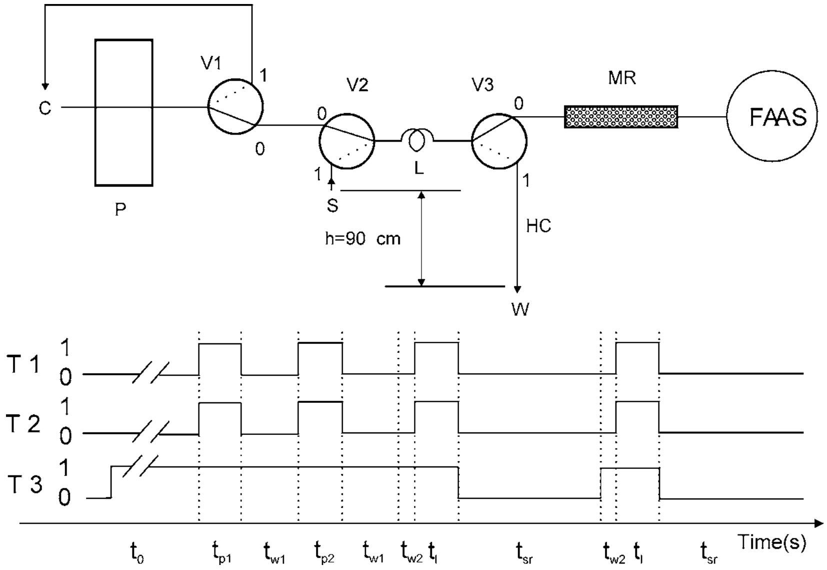

Fig. 1. Flow system diagram and valves timing course. P: peristaltic pump; V1, V2, V3: solenoid valves; L: sample loop (0.8 mm i.d. Teflon FEP tubing, 6 cm long); C: deodorised kerosene, 6.9 mL min^{-1}; MR: packed mixing reactor; FAAS: flame atomic absorption spectrometer; HC: hydrostatic column; W: waste; T$_1$, T$_2$ and T$_3$: switching timing course for valves V$_1$, V$_2$ and V$_3$, respectively. The time intervals t_0, t_{p1}, t_{p2}, t_{w1}, t_{w2}, t_l and t_{sr} are defined in the text.

The mixing reactor (MR) was coupled to the inlet of the spectrometer (FAAS) nebuliser. In this configuration, all valves are switched off and only the carrier fluid (C) is pumped towards the spectrometer (FAAS).

The operation of the system comprised a normal analytical cycle, when the same sample was repeatedly injected and measured, and a special cycle when samples were changed. When the software was run, the personal computer requested the control parameters. Afterwards, it sent the control commands through the LPT1 port to switch on/off valves V_1, V_2 and V_3 following the switching pattern depicted in the valves timing course in Fig. 1. This was done maintaining the bits d_0, d_1 and d_2 of the LPT1 port at high TTL level during the time intervals previously established. At the beginning of the work, valve V_3 was switched on during a time interval t_0 (90 s) to fill the hydrostatic column with the carrier fluid (C).

When a new sample was processed, the system carries out a special purge cycle for 60 s in order to clean and fill the intake tubing and V_2 with the new sample. For this purpose, V_1, V_2 and V_3 were energised for 15 s (t_{p1}). During this period, solvent (kerosene) was aspired through the sample intake tube. Afterwards, V_1 and V_2 were switched off for 15 s (t_{w1}); during this time, the solvent was manually replaced by the new sample in the intake tube, and then V_1 and V_2 were switched on again and new sample aspirated into the system for 15 s (t_{p2}). This procedure was performed to minimize the possible existence of memory effects. To complete the purging cycle valve V_3 was maintained switched on (while V_1 and V_2 were switched off) during the time interval of 15 s (t_{w2}) to wash the sampling loop (L) with the solvent fluid (C).

At all instances when sample was inserted in the loop L, solvent is recycled to the bottle and thus carrier feeding to the AAS spectrometer is interrupted. The same is true during t_0 when solvent is loaded into the hydrostatic column, but in this instance no recycling occurs.

The normal analytical cycle begins turning on V_1, V_2 and V_3 for 15 s (t_l) to fill the sampling loop with sample. Afterwards, V_1, V_2 and V_3 were turned off during the signal recording time (t_{sr}), which was set at 50 s. In this time period, the carrier fluid (C) flowed again through the normal path, and the sample plug was displaced into the packed mixing reactor where it was intimately mixed with the carrier and transported to the nebuliser of the AA spectrometer. After this time, a new analytical cycle was carried out to complete the replicates established in the set-up table when the control software was run. In this case, it was not necessary to carry out the purging cycle.

Before the next repetition of the sample processing, V_3 is turned on for 5 s (t_{w2}) in order to introduce a small solvent segment into the hydrostatic column. This was found necessary in order to ensure a smooth motion of the fluid within the hydrostatic column.

Under this conditions, calibration curves were obtained by processing five standard solutions (plus a blank) prepared as described above. Typical signals from a calibration curve and blank can be seen in Fig. 2.

3. Optimisation of loop length and filling time

Using the gravitational force to displace the sample, the flow rate obtained depends on the viscosity of the fluid being impelled as well as height and inner diameter of the hydrostatic column (HC). The optimisation procedure took sample viscosity into account, aiming to establish the conditions that minimized the effect of this variable on the mea-

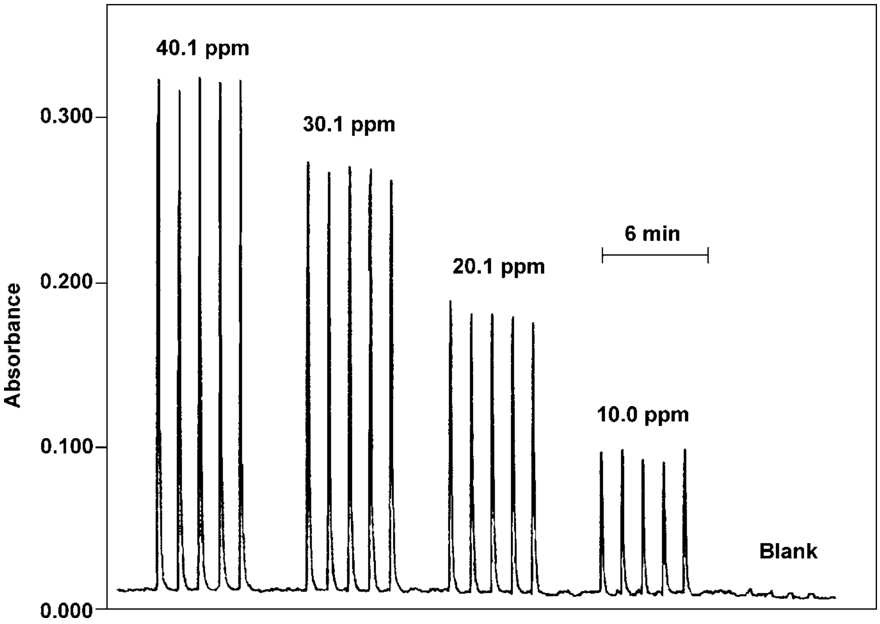

Fig. 2. Recording of the analytical signals using copper ($\lambda = 324.7$ nm) from a calibration curve plus blank.

surements. Four synthetic mixtures were prepared encompassing the viscosity range from 75 to 165 cSt (at 40 °C). This is a typical viscosity range for internal-combustion engine lubricating oils. The mixtures were prepared by accurately weighing variable amounts of Conostan BO75 oil, Superdiesel 40 oil (ANCAP) and Conostan S-21 multielemental standard in order to produce a final metal concentration of ca. 30 ppm. The Superdiesel 40 oil was checked to certify that it was free from the four metals (Fe, Cu, Pb, Cr) to be determined. The BO75 was certified metal-free from factory. Viscosities of the two oils were measured according to ASTM standard D-445, while viscosities of the mixtures were calculated by means of a suitable nomograph.

The assays to define the loop length and to find the interval to fill it with sample fluid were accomplished using copper as a model analyte and thus the AAS spectrometer was set up at 324.7 nm.

The variables studied were sampling loop length (4, 6 and 8 cm) and loading time. These assays were carried out using the four synthetic sample mixtures and for each sampling loop the loading time intervals were varied from 5 to 25 s with increment of 5 s. Instrumental response (peak height, absorbance) was normalised with respect to actual metal concentration of the mixture being injected. This strategy was necessary because the mixtures were prepared by weight and thus the concentrations, although very close to 30 ppm, were slightly different from one solution to the other. Each synthetic mixture was injected five times and the results averaged.

3.1. Carryover

Prior to process, the new sample the purging cycle described in the flow system section was carried out to minimise the carryover effect that could occur because of the high viscosity of the samples. In order to investigate the effectiveness of the proposed strategy, an oil standard solution containing a copper concentration of 30.1 ppm was injected followed by the injection of an oil blank sample.

3.2. Reference method

The metal contents of the samples were measured by atomic absorption spectrometry after dilution 1 + 4 (w/w) with kerosene. Sample preparation by weight is mandatory according to the ASTM standard cited above [4]. This is the method employed in the actual practice for the determinations of wear metals in many laboratories.

4. Results and discussion

4.1. Hydrostatic column

In preliminary experiments, it was observed that peristaltic pumps were not appropriate to propel samples presenting high viscosity. The difficulties comprised variation of flow rate and long washing time, thus lessening both precision of measurements and throughput. In earlier work, this disadvantage was surmounted using a mechanised gas-tight syringe approach [15]. In this work, the flow system was designed to carry out the sampling step by displacing sample fluid by gravity aiming to improve the system simplicity avoiding the use of mechanical devices.

Previous assays showed that the stream caused by gravity action does not ensure a constant flow rate when highly viscous samples are handled. Additional experiments showed that the insertion of solvent segments into the sample bulk contributed to attain a smooth and uniform motion of the oil segments. The necessary segmentation (solvent–oil–solvent) was easily implemented by enabling the control software without any modification of the proposed flow system configuration following the valves timing course depicted in Fig. 1.

5. Determination of the optimum loop length and filling time

In the proposed flow system, the sampling flow rate was affected by sample viscosity and length of sampling loop and as a consequence affecting also the time interval necessary to fill the loop with sample. In this sense, experiments were carried out aiming to find the combination of sampling loop length and filling time that minimised the influence of viscosity on the measurements and results are shown in Table 1. The loading time and loop length producing the smaller relative signal difference (range) between samples of different viscosity was chosen.

Analysing these data, it can be observed that the minimum relative range (i.e. variation) in the response was obtained with a loop length of 6 cm and loop filling time intervals of 15 and 20 s presenting as results relative variation, 2.4% and 2.3%, respectively, a loop filling time of 20 s (2.3%). However, with 15 s, the range is almost as low (2.4%). Since the results were similar, the time interval of 15 s was selected and loop length of 6 cm were chosen.

Under these operating conditions, a maximum relative difference of 2.4% was found between results provided by samples of different viscosity. This represents the maximum variation in the results that could arise from samples con-

Table 1
Data corresponding to the relative range (%) of the responses (peak height and absorbance) obtained by analysing four different artificial oil samples with viscosities in the range 75–165 cSt.

Sampling loop length (cm)	Sampling loop loading time (s)				
	5	10	15	20	25
4	29.1	4.4	5.5	2.8	2.5
6	44.0	13.2	2.4	2.3	7.4
8	27.4	13.5	3.0	3.3	6.6

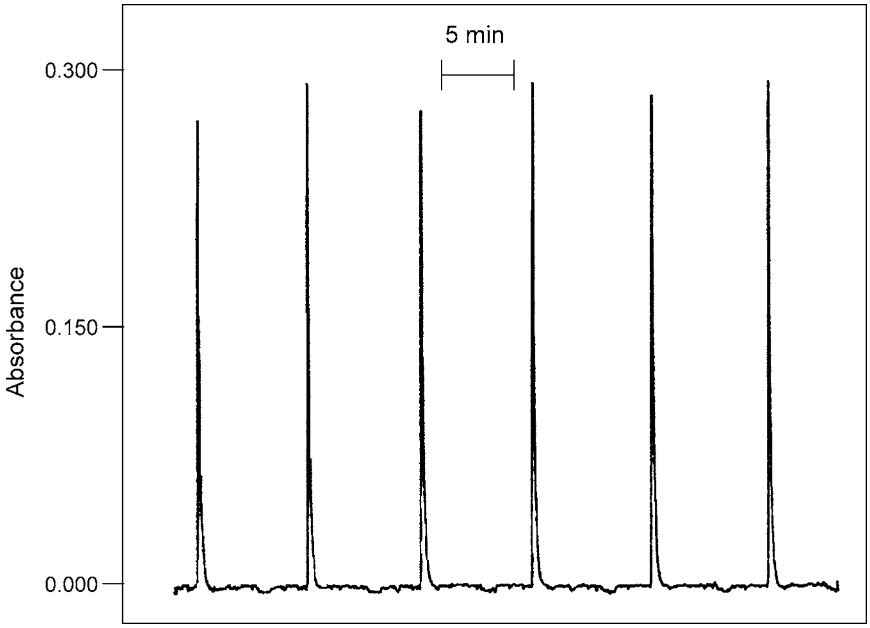

Fig. 3. Recording of the signal in the experiment for assessing carryover effects. Samples used were a 30 ppm (w/w) copper standard solution and a blank oil sample, which were injected alternately six times and signal was monitored at $\lambda = 324.7$ nm.

taining the same metal concentration but different viscosities and is also an estimation of the robustness of the method for this variable. This variation is acceptable for this of application.

6. Carryover

High viscosity is an inherent feature of the oil samples that could impair the precision of the measurements. To overcome this drawback, assays were performed settling the purging cycle at 60 s ($t_{p1} + t_{p2} + 2t_{w1}$, see Fig. 1) and inserting alternately a 30.1 ppm (w/w) copper standard solution and an oil blank sample. Results of the corresponding test presented in Fig. 3 show that between two subsequent measurements related to copper standard solution, no significant record that could be related to the oil blank sample was detected; in this sense, indicating that the purging cycle at 60 s was enough to clean the intake tube of valve V_2.

7. Validation

The proposed method was validated for four metals (Cu, Cr, Fe, Pb). Figures of merit studied were linearity of the calibration curves, accuracy and precision.

Linearity was studied in the range 0–40 ppm (Cu, Fe) and 0–15 ppm (Cr, Pb), selected to span the concentration ranges expected in real samples. The relation between response (peak height and absorbance) and concentration was subject to linear regression analysis yielding the results showed in Table 2. In all instances, a linear fit was found to be adequate for the purpose.

Accuracy was assessed by comparison of the results obtained with the proposed procedure and those obtained by flame atomic absorption spectrometry performed in batch. Each sample was analysed for the four metals by the proposed method (five replicates) and by the batch FAAS method. The results obtained by the two methods were compared by means of a correlation graph using a linear model. The slope and the intercept of the straight line were compared with the theoretical values (one and zero) by means of the joint-confidence region (or joint-confidence ellipse) test [21], and results are summarised in Table 3. At the confidence level of 95%, no significant difference was found between the results obtained by the proposed system and the reference method.

The precision that could be attainable employing the proposed system was evaluated by the determination of copper as a model analyte. Relative standard deviations (five replicates) obtained for the calibration curve (10, 20, 30 and 40 ppm) were 0.9%, 1.7%, 0.5% and 1.2%, respectively. The results of copper determination in real samples of used oil, where concentration varies widely, showed that relative standard deviation varied in the range of 0.5%–5.3% ($N = 5$).

Table 2
Regression parameters related to calibration curves of copper, chromium, iron and lead

Metal	Slope (ppm^{-1})	Intercept	R^2
Cu	0.0117	0.0119	0.9972
Cr	0.0058	0.0023	0.9976
Fe	0.0062	0.0127	0.9977
Pb	0.0022	0.0059	0.9938

Table 3
Results of the joint-confidence ellipse *F*-test for the regression straight line obtained for copper, iron, chromium and lead

Parameter	Cu	Fe	Cr	Pb
a' (ppm)	−0.089	1.561	0.041	1.881
b'	0.956	0.861	0.944	0.796
F exp.	2.48	1.932	1.544	4.695
$F_{0.05}$	3.885	3.739	3.493	4.737
N	14	16	22	9
Result	Passes test	Passes test	Passes test	Passes test

$x_1 = a' + b'x_2 \quad H_O : a' = 0 \text{ and } b' = 1 \quad H_A : a' \neq 0 \text{ or } b' \neq 1$
x_1: result (ppm) obtained with proposed method; x_2: result (ppm) obtained with reference method; F exp.: experimental value of F-statistic; $F_{0.05}$: value of F-statistic at 95% confidence level; N: number of samples analysed.

For the other metals, especially for chromium and lead, precision was poorer, typically in the range 3%–8%, but these results could be expected considering that concentrations and absorbances were very low (absorbances under 0.04 for lead and under 0.09 for chromium). Anyhow, this is not a serious drawback given the way the analytical data are used in engine fault diagnosis.

8. Conclusions

Handling of highly viscous samples of lubricating oils in flow systems has always been a challenge. The results obtained in this work suggest that the use of a multicommutation approach along with gravity drive is promising, therefore, its association can provide an useful means for automation of the analytical procedure for the determination of other analytes in oil samples.

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References

[1] M. Lukas, D.P. Anderson, Lubr. Eng. 54 (1998) 19.
[2] M. Lukas, D.P. Anderson, Lubr. Eng. 54 (1998) 31.
[3] Book of ASTM Standards, Method D-5184-91, Section 5, V. 5.03, American Society for Testing and Materials, Philadelphia, PA, USA, 1992.
[4] Book of ASTM Standards, Method D-5185-91, Section 5, V. 5.03, American Society for Testing and Materials, Philadelphia, PA, USA, 1992.
[5] Book of ASTM Standards, Method D-4927-89, Section 5, V. 5.03, American Society for Testing and Materials, Philadelphia, PA, USA, 1992.
[6] J. Ruzicka, E. Hansen, Flow Injection Analysis, second ed., Wiley, New York, 1989.
[7] S. Hirata, T. Kajiya, N. Takano, M. Aihara, K. Honda, O. Shikino, E. Nakayama, Anal. Chim. Acta 499 (2003) 157.
[8] P. Mikuska, Z. Vecera, Anal. Chim. Acta 495 (2003) 225.
[9] A.P. Packer, A.P.G. Gervasio, C.E.S. Miranda, B.F. Reis, A.A. Menegario, M.F. Giné, Anal. Chim. Acta 485 (2003) 145.
[10] A.P.G. Gervasio, G.C. Luca, A.A. Menegario, B.F. Reis, H. Bergamin, Anal. Chim. Acta 405 (2000) 213.
[11] J.L. Burguera (Ed.), Flow Injection Atomic Spectroscopy, Dekker, New York, 1989.
[12] A. Sanz Medel (Ed.), Flow Analysis with Atomic Spectrometric Detectors, Elsevier, Amsterdam, 1999.
[13] B. Welz, M. Sperling, Atomic Absorption Spectrometry, third ed., Wiley–VCH, Weinheim, 1999.
[14] M.P. Granchi, J.A. Biggerstaff, L.J. Hilliard, P. Grey, Spectrochim. Acta B 42 (1987) 169.
[15] G. Pignalosa, M. Knochen, At. Spectrosc. 22 (2001) 250.
[16] T.V. Liston, Lubr. Eng. 48 (1992) 389.
[17] F.R.P. Rocha, B.F. Reis, E.A.G. Zagatto, J.L.F.C. Lima, R.A.S. Lapa, J.L.M. Santos, Anal. Chim. Acta 468 (2002) 119.
[18] R.N. Fernandes, B.F. Reis, Talanta 58 (2002) 729.
[19] C.K. Pires, B.F. Reis, C.X. Galhardo, P.B. Martelli, Anal. Lett. 36 (2003) 3011.
[20] J.A. Vieira, I.M. Raimundo, B.F. Reis, M.C.B.S.M. Montenegro, N.N. Araujo, J. Braz. Chem. Soc. 14 (2003) 259.
[21] J. Mandel, F.J. Linnig, Anal. Chem. 29 (1957) 743.