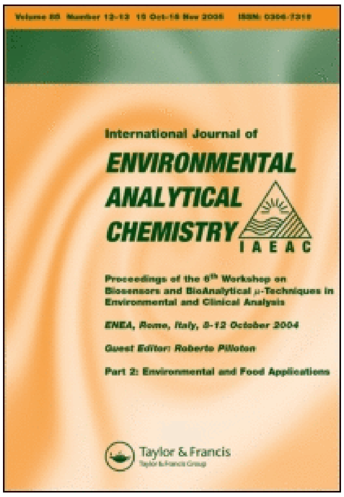

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DETERMINATION OF HEAVY METALS IN WASTE LUBRICATING OILS BY INDUCTIVELY COUPLED PLASMA–OPTICAL EMISSION SPECTROMETRY

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In accordance with EU strategy on waste, the utilization of waste oils as a fuel in local power plants has become an interesting choice in hazardous waste treatment planning. The present requirement in Finland is that all oil batches to be burned in power plants must be analyzed for six heavy metals. Thus rapid and cheap methods are needed for these analyses. We have studied and optimized the analytical conditions in the use of sequential inductively coupled plasma–optical emission spectroscopy (ICP-OES) for the quantitative determinations of heavy metals (Cd, Cr, Cu, Ni, Pb, V) in waste lubricating oils. The study showed that using the proposed kerosene dilution method, waste oils can easily be analyzed for heavy metals and the analytical performance of the method is good. In addition, the results suggest that, at least in the case of the Oulu Municipal Waste Management the use of a pair of indictor metals should be sufficient for required determination of heavy metals.

Keywords: ICP-OES; Heavy metals; Waste oil; Kerosene dilution method

INTRODUCTION

According to the present EU strategy on waste (in Finland since 1996) and in accordance with the principle of sustainable development, hazardous waste materials and other chemical waste should be eliminated as near as possible to the place of origin. Thus the possibility of the utilization of

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*Corresponding author. Fax: +358-8-5531608. E-mail paavo.peramaki@oulu.fi waste oils as a fuel in local power plants has become an interesting choice in hazardous waste treatment planning in Finland. Local combustion is also a logistically reasonable alternative in contrast to the old fully centralized combustion in countries (e.g. Finland) where the distances are long. The prevailing situation in Finland is nevertheless complicated by the present requirement that all oil batches to be burned in power plants must be analyzed for the following six metals: Cd, Cu, Cr, Ni, Pb and V [1,2].

A rapid method is needed for monitoring the heavy metal concentrations in the waste lubricating oils to be burned. Inductively coupled plasma–optical emission spectrometry (ICP-OES) has proved to be a reliable technique for element determinations in a variety of samples. The technique can also be applied in the analysis of waste oil samples. Before the measurements, the samples must be diluted with an organic solvent, such as xylene [3,4] kerosene [5] or MIBK [6,7]. One advantage of using kerosene is its low volatility (when compared to xylene, for example). Calibration standards are prepared from organometallic standards and diluted with the same solvent as the sample. The advantage of this direct method is that there is no need for any sample decomposition step before the analysis.

The applicability of the sequential ICP-OES technique for waste lubricating oil analysis was studied in this work. One scope of this study was to find, if possible, a pair of indicator metals that would reflect the general status of the heavy metal concentrations and their possible correlations in the common waste oil batches collected in the local municipal waste management in Oulu. This would further simplify and speed up the analytical procedure. For the use of waste management this idea must be tested in the future more widely in the other corresponding cases.

EXPERIMENTAL

Sampling of the Waste Lubricating Oils

Waste oil samples were taken from four large (30 m^3) reservoirs (oil–water phase formation), situated in the Oulu municipal waste management plant, and placed in 250 or 500 ml acid washed polyethylene bottles. Two samples were combination samples from two different reservoirs, taken from three different heights (bottom, middle, top). This was easily achieved since the tanks were equipped with three stopcocks at different heights. Separate samples were taken from each height in order to study the homogeneity of the waste oil in two large tanks. In addition, three samples were taken from smaller separate batches (4, 10 and 200 dm^3), to check the general quality of the waste lubricating oils.

Sample Preparation and Determination by ICP-OES

Calibration solutions for Cd, Cr, Cu, Ni, Pb and V were prepared using commercial Conostan-S21 standard oil (Conoco Speciality Products, Inc.) that contained 500 mg/kg of each element studied. Working standards containing 5, 25, 50 and 100 mg/kg of the metals were prepared by diluting the standard oil with Conostan-20 base oil. The calibration solutions (0.5–10 mg/kg) were prepared by weighing 2 g of working standards and diluting them with kerosene (Fluka, purum) in order to obtain a total weight of 20 g (1 : 9 w/w ratio of oil/kerosene).

The samples were prepared similarly to calibration standards 1 : 9 w/w ratio). Thus the oil concentration in each sample and standard was the same. Before the measurements, the coarse particulate matter was separated from the diluted samples by centrifugation (MSE: 2500 rpm, 1 min). This had little or no effect on recoveries of the metals studies (see Results and Discussion). Centrifugation is necessary because the coarse particles might block the sample introduction system of the ICP-OES instrument.

A sequential Pye Unicam 7000 inductively coupled plasma optical emission spectrometer equipped with a Gilson 221 autosampler was used for the determination of the six metals mentioned above in the waste lubricating oils. The design of the spectrometer includes an echelle grating for wavelength separation, and a grid nebulizer for sample aspiration. Optimized operating parameters and spectral lines used in oil analyses with the kerosene dilution method are given in Table I.

RESULTS AND DISCUSSION

Optimization of the ICP-OES Instrumental Parameters using Statistical Experimental Design

Statistical experimental design was used in the optimization of the analytical method. With the aid of statistical experimental design it is possible to screen out for the most important factors (and their statistical significance) that affect the responses of the metals studied. The following instrumental parameters were investigated: plasma power, the flow rate of the auxiliary argon, sample introduction rate, nebulizer pressure and sample viscosity.

TABLE I Optimized operating conditions and the spectral lines used in the analysis of kerosene diluted samples by sequential ICP-OES

Parameter	*Settings*	*Metal*	*Spectral line* (nm)
Generator power	1.0 kW	Pb	220.353
Coolant flow	13 L min^{-1}	Cd	214.438
Auxiliary flow	0.2 L min^{-1}	Cu	324.754
Sample uptake	0.85 g min^{-1}	Ni	231.604
Nebuliser pressure	170 kPa	V	310.230
Optimize element	Pb	Cr	206.149

TABLE II Two level factorial design used for the optimization of the ICP-OES method

Factor	*Low level*	*High level*
Power (kW)	0.9	1.5
Nebulizer pressure (kPa)	170	240
Auxilliary argon flow (L min^{-1})	0.2	1.0
Sample uptake rate (g min^{-1})	0.75	0.85
Sample viscosity/relative amount oil/kerosene	0.1	0.2

A two level factorial design (2^5-experiment) was used, i.e. each factor was studied at its low and high levels (Table II). In addition, three replicates were made in the centerpoint of the design in order to obtain an estimate of the experimental error. The response optimized was SBR (net signal to background-ratio). The standard solution used in optimization experiments contained 10 mg kg^{-1} of each element (sample preparation: 1 : 9 w/w ratio of oil/kerosene). The total amount of experiments was 70. The analytical data obtained was processed using a commercial computer software package Modde 3.0 for Windows and the responses were fitted using first order functions [8].

The experimental design showed that the most important factors that affect the SBR values of the elements were nebulizer pressure and the flow rate of the auxiliary argon. In each case, the best SBR values were obtained when the factors were at their lower levels. Although according to the model, the best analytical results were obtained without an addition of the auxiliary argon, the auxiliary argon flow of 0.2 L min^{-1} was used to prevent carbon residue build up on the tip of the injector tube when an organic solvent is used. The plasma power had a significant effect only in the determination of copper, nickel and vanadium; SBR-ratios increased at the lower plasma power. Sample introduction rate and sample viscosity had minor effects that could not be distinguished from the experimental errors. Therefore, the effect of sample viscosity was studied separately (see Interference Effects in the Procedure).

The sensitivity for lead was the worst among the metals studied in this work. Therefore, the instrumental parameters for routine measurements were selected so that the SBR for lead was as high as possible, yet the sensitivity for the other elements was still satisfactory (Table I). Due to the poor sensitivity of lead, Pb 220.353 nm was used in the optimization of the viewing height in the plasma before each measurement sequence.

Interference Effects in the Procedure

Generally, the ICP-OES technique is considered to be relatively free from chemical interferences when compared to the other atomic spectrometric techniques. In practise, chemical interferences can still occur but to a lesser extent due to the very high temperature of the plasma source. The interference effects can be divided into those arising from the sample introduction, and the matrix effects in the plasma. Spectral interference is a potential source of interferences due to a very rich line spectra in the plasma. However, scans of the spectral profiles around the emission lines showed that no spectral interferences were present in the oil samples analyzed in this work.

Sample introduction is prone to interference caused by the different physical properties of the samples and standards, namely viscosity and surface tension. The samples and standards are aspirated into the plasma at different rates, which results in systematic errors. The effect of sample viscosity on the SBR-ratios of the different elements was studied by analysing samples containing the same concentration ($10\,\mathrm{mg\,kg^{-1}}$) of the elements, but a different viscosity (i.e. the mass ratio oil/kerosene was changed). The samples were prepared using Conostan-S21 standard oil and a metal free Conostan-20 dilution oil. The effect of dilution was similar for all the elements studied. The increase in the amount of dilution oil from one-tenth to one-fifth lowered the SBR-ratios about 5–10% (Fig. 1).

When long sample series were analyzed, a carbon residue built up on the tip of the injector tube. This was partly avoided when the plasma torch was lowered 2–3 mm from its usual position inside the induction coil. Thus the carbon build up was significantly diminished due to the lower temperature at the injector tube tip. Auxiliary argon flow ($0.2\,\mathrm{L\,min^{-1}}$) was also necessary to diminish the effect. The residue build up also depended significantly on the dilution ratio of the sample. When the dilution ratio was 1/5,

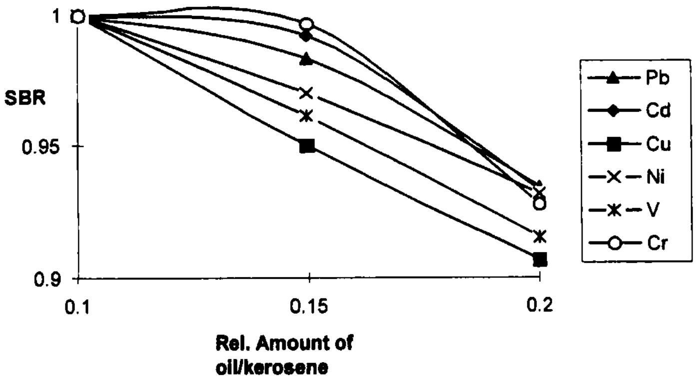

FIGURE 1 The effect of sample viscosity on the SBR-ratios of the different elements ($n = 3$). The scaled SBR-values are shown on the y-axis. The value 1.0 is given for the most dilute sample (dilution factor 0.1).

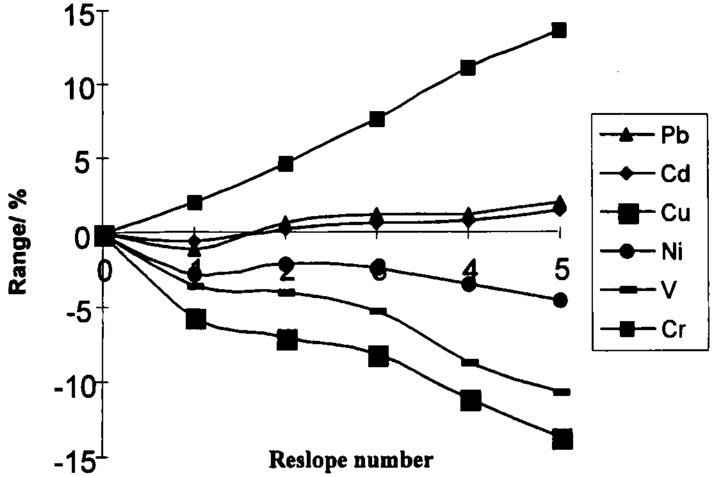

FIGURE 2 Drift of the slope of calibration functions over 3 h measuring period (5 reslope measurements at regular intervals in 3 h).

the plasma was even extinguished. Even a small carbon residue build up has a harmful effect on the ICP-OES stability and causes drift. The largest drift was observed for chromium and copper. The slope of the calibration function changed 15% during the 3 h measuring period (Fig. 2). Due to the drift of the measuring system, it was necessary to update the calibration function after measuring each 5–8 sample batches.

The waste lubricating oils analyzed usually contain considerably large amounts of solid particulate matter that may cause blockage of the sample introduction system of the ICP-OES, and should therefore be removed. However, the removal of solid particles may cause systematic errors, since the metals analyzed may be associated with these solid particles and are thus not recovered in the analysis. Hence, false analytical results are obtained. Three pretreatment steps for the waste oils were investigated. These included normal filtration with Whatman paper (no: 41, fast), membrane filtration (Gelman Sciences, 0.2 µm) and centrifugation (MSE: 2500 rpm, 1 min). The results obtained after paper and membrane filtration were clearly lower than those obtained for the samples that were centrifuged. Thus centrifugation reliably removed the heaviest particles and yet had little or no effect on the recoveries of the metals studied. To obtain an estimate of the bias caused by the removal of solid particles by membrane filtration, the metal concentrations in the residues were determined after decomposition the membranes with concentrated sulphuric acid and 30% H_2O_2. The metals associated with the particles larger than 0.2 µm generally caused a bias of 5% in the results (Table III). Ten elements were also determined qualitatively from the residue (Table IV).

Analytical Performance of the Proposed Method

The concepts often referred to in connection with instrumental techniques are the linear dynamic range (LDR), the limit of detection (LOD) and the limit of quantification (LOQ). Of course the analytical procedure should also be accurate, i.e. systematic errors should not exist. In this work the following recommendations were used to determine the detection power

TABLE III Quantitative analysis of the solid residue obtained after 0.2 µm membrane filtration[a]

Sample	*Solids* %	*Pb*/mg g^{-1} *(bias %)*	*Cu*/mg g^{-1} *(bias %)*	*V*/mg g^{-1} *(bias %)*	*Cr*/mg g^{-1} *(bias %)*
5.8.-97 S2C	0.41	0.143 (0.9%)	0.063 (1.5%)	0.073 (4.9%)	0.035 (4.6%)
5.8.-97 S2A	0.28	0.221 (0.8%)	0.054 (0.8%)	0.087 (3.9%)	0.034 (3.1%)
27.8.-97 S2C top	0.33	0.167 (0.8%)	0.127 (2.3%)	0.130 (5.7%)	0.039 (4.0%)
27.8.-97 S2C middle	0.45	0.157 (1.0%)	0.054 (1.4%)	0.044 (2.1%)	0.037 (4.8%)
27.8.-97 S2C bottom	0.49	0.125 (0.9%)	0.101 (2.8%)	0.074 (3.9%)	0.053 (7.4%)

[a] Ni and Cd were not found.

TABLE IV Qualitative analysis of the solid residue obtained after membrane filtration (0.2 μm)

Element measured[a]	*Emission line*/nm	*Result (yes/no)*	*Limit of detection*/mg kg^{-1}
Zinc	Zn 213.856	Yes	10
Iron	Fe 259.940	Yes	10
Molybdenum	Mo 202.030	No	15
Aluminium	Al 308.215	No	25
Calcium	Ca 393.366	Yes	1
Zirconium	Zr 339.198	No	10
Magnesium	Mg 279.553	Yes	2
Cobalt	Co 228.616	No	10
Tin	Sn 189.926	No	200
Arsenic	As 193.695	No	200

[a] In aqueous solution.

of the method towards different metals: $\mathrm{LOD} = c_{\mathrm{blank}} + 3\,\mathrm{sd}_{\mathrm{blank}}$ and $\mathrm{LOQ} = c_{\mathrm{blank}} + 10\,\mathrm{sd}_{\mathrm{blank}}$, where c_{blank} is the average result for the blank determinations and $\mathrm{sd}_{\mathrm{blank}}$ is the standard deviation of the blank determination (five replicates). The limit of quantification is a lowest concentration where a satisfactory precision (often 10%, expressed as relative standard deviation, RSD) is obtained. LOD and LOQ are not absolute concentrations. They are very dependent, for example, on the analytical performance of the ICP-OES instrument at each day. Therefore, these figures of merit are not be taken too literally.

Method LOD and LOQ should be determined over a long period of time and a large amount of statistical data should be collected. In this work the limit of detection and quantification were based on the results obtained on three different days (5 blank determinations per day). The average method detection limits using sample dilution of 1/10 (1 : 9 w/w ratio of oil/kerosene) are shown in Table V.

The linear dynamic range of the method was studied by measuring calibration solutions in the concentration range of 5–500 mg kg^{-1} for all six metals studied. Inspection of the residuals showed that the linear model was correct at least in the range studied; the limit of detection can be considered as the lower limit of the range. Sensitivities for the different elements varied considerably when the compromise conditions were used. The sensitivity was best for Cu and worst for Pb.

To estimate the different sources of variability (repeatability) of the method presented here the measurements were made from the same sample on three successive days. Five replicate samples were analyzed at each day. In addition, three repetitions were made from each sample on

TABLE V Method detection limits and quantification limits obtained by ICP-OES

Element	*Detection limit*/mg kg^{-1}	*Quantification limit*/mg kg^{-1}
Pb	2.1	3.2
Cd	1.1	1.2
Cu	0.8	1.1
Ni	1.2	1.5
V	0.5	0.7
Cr	1.0	1.5

TABLE VI Sources of variability in metal analysis by ICP-OES ($p = 0.05$)

Analyte	*Between days* s_b/%	*Sample preparation* s_v/%[a]	*Random variation* s_o/%	*Total variation* s_t/%
Pb	1.84	ns	2.58	3.17
Cd	1.95	ns	2.33	3.03
Cu	ns[a]	1.48	1.75	2.29
Ni	3.01	ns	1.82	3.51
V	3.04	1.24	1.66	3.68
Cr	2.56	ns	1.64	3.04

[a] ns = not significant.

any particular day. The total variance of the result can be broken into the three different components [9]: $\sigma_t^2 = \sigma_o^2 + \sigma_v^2 + \sigma_b^2$. Here σ_o^2 = random error, σ_v^2 = variance of interaction (sample preparation and the equipment) and σ_b^2 = variance due to systematic errors between different days.

The variance estimates for the different components are calculated and tested. σ_v^2 and σ_b^2 are compared to σ_o^2 and it is decided whether they differ significantly from zero (the Fisher *F*-test is applied). The results for the different variance components for each element are shown in Table VI. The results showed that total uncertainty of the method varied between 3.0–3.7%.

Determination of Metal Contents in Waste Oils

The proposed kerosene dilution method allows an easy way to monitor the quality of waste lubricating oils and their suitability for energy production in power plants. Four large reservoirs (30 m^3) and three small containers from the Oulu Municipal Waste Management plant were analyzed (Table VII and Fig. 3). The results in Table VII indicate that, according to EU regulations and strategy, the waste oil could be burned in local

TABLE VII Metal contents in waste oils at different depths (n = number of samples)

Sample	*Pb*/mg kg^{-1} $n=3$	*Cd*/mg kg^{-1} $n=3$	*Cu*/mg kg^{-1} $n=3$	*Ni*/mg kg^{-1} $n=3$	*V*/mg kg^{-1} $n=3$	*Cr*/mg kg^{-1} $n=3$
1. 30 m^3 top	72 ± 1	2 ± 2	18 ± 1	4.1 ± 0.5	8 ± 1	3.2 ± 0.5
1. 30 m^3 middle	68.9 ± 0.4	2 ± 1	18 ± 1	4.8 ± 0.8	9 ± 1	3.5 ± 0.6
1. 30 m^3 bottom	66 ± 1	2 ± 1	17.7 ± 0.6	4.8 ± 0.60	9.2 ± 0.8	3.5 ± 0.2
Average	68.8	2.1	17.9	4.6	8.6	3.4
2. 30 m^3 top	68 ± 2	3 ± 1	23.0 ± 0.9	3.6 ± 0.7	6.1 ± 0.1	3.2 ± 0.3
2. 30 m^3 middle	71 ± 2	2.2 ± 0.9	24.1 ± 0.7	3.5 ± 0.6	6.2 ± 0.1	3.5 ± 0.3
2. 30 m^3 bottom	73.6 ± 0.9	3 ± 2	24.2 ± 0.5	3.7 ± 0.5	7.0 ± 0.1	3.9 ± 0.6
Average	70.7	2.5	23.8	3.6	6.4	3.5
3. 30 m^3 (comb.)	65 ± 2	2.4 ± 0.4	17 ± 1	3.4 ± 0.5	6 ± 1	3.1 ± 0.5
4. 30 m^3 (comb.)	73.8 ± 0.8	2 ± 1	19 ± 1	3.5 ± 0.5	6 ± 1	3.1 ± 0.4
smaller batches						
5. 4 dm^3	47 ± 3	4 ± 2	8.3 ± 0.4	< 1.5[a]	< 0.7[a]	< 1.5[a]
6. 10 dm^3	6 ± 5	3 ± 1	85 ± 3	< 1.5[a]	< 0.7[a]	< 1.5[a]
7. 200 dm^3	265 ± 20	4 ± 1	22.2 ± 0.3	< 1.5[a]	< 0.7[a]	< 1.5[a]

[a] Under quantification limit.

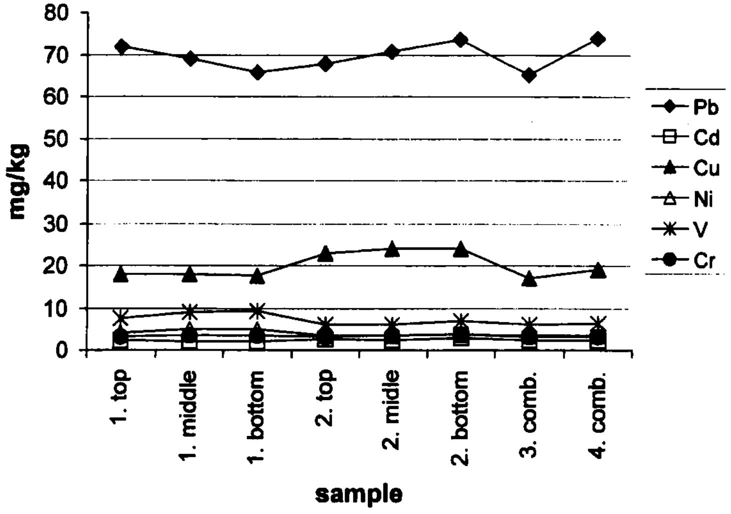

FIGURE 3 Concentration of heavy metals in waste lubricating oils. For explanations of samples, see Table VII.

power plant. The maximum limits for the different heavy metals in the emission gases are reported in Refs. [1,2]. When unknown samples are analyzed, recovery tests are a vital part of the work when an analytical procedure is developed. Interference effects existing in sample introduction and in the plasma can be discovered by recovery tests. The sample matrix was spiked

TABLE VIII Results of the recovery tests from waste lubricating oil

Analyte	*Recovery/%(n = 15)*
Pb	89.8 ± 3.4
Cd	90.0 ± 2.3
Cu	88.9 ± 3.7
Ni	92.5 ± 2.4
V	92.9 ± 3.4
Cr	93.1 ± 2.4

using Conostan-S21 standard (300 or 500 mg kg^{-1}). Recoveries for all the elements studied were about 90% which is satisfactory for quantitative work (Table VIII).

CONCLUSIONS

One aim of this study was to find a pair of indicator metals whose concentration in waste oil would reflect the concentrations of the other elements of interest. Thus, the quality control of the oil batch would be greatly simplified. Although the amounts of metals in small waste containers varied, the amount of every metal studied from the large reservoirs was practically independent of the batch studied and the depth in the reservoir (top, middle, bottom). The confidence intervals for different elements indicate that only in the case of lead and vanadium the concentrations of these elements are dependent on the sampling depth. In the case studied here, determination of a pair indicator metals should be enough to estimate the total amounts of heavy metals present in waste lubricant oils before burning them in power plants. The indicator metals may be one or two of the metals lead, copper or vanadium. The size of statistical population at this point is not large enough, and thus very strict conclusions cannot be drawn. Of course, in different cases the indicator metals may be different and we are planning to investigate also other waste oils in Finland to clarify this topic.

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