

Analysis of liquid hazardous waste fuels (LHWF) per ASTM D5839 with ARL QUANT'X EDXRF Spectrometer

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Introduction

Liquid hazardous waste is an industrial waste typified by mixtures of solvents, oils, paints and pigments which may pose a potential hazard to human health or the environment when improperly disposed of. Such waste is often non-homogeneous, may be a single phase or multiphase liquid, and often contains suspended solids. When recycling is not an option, the preferred disposal route is to recover the inherent energy by using the waste as an alternative fuel in industrial furnaces. Before incineration, it is usually required by governmental regulations to screen such liquid hazardous waste fuel (LHWF) for the presence of toxic and/or volatile elements above certain concentration levels.



ASTM D5839 describes a method for the determination of trace element concentrations by Energy-Dispersive X-Ray Fluorescence (EDXRF) in typical LHWF used by industrial furnaces. A total of 11 elements--Ag, As, Ba, Cd, Cr, Hg, Ni, Pb, Sb, Se, and Tl--can be monitored over a wide concentration range from ppm to % w/w. Because of potential elemental spectral line overlap, an X-ray detector with adequate resolution is preferred.

The Thermo Scientific™ ARL™ QUANT'X Spectrometer equipped with a state-of-the-art Silicon Drift Detector (SDD) offers the necessary resolution to minimize or eliminate effects of spectral interference. This study describes the analysis of a subset of 6 elements of interest (Ag, Cd, Cr, Ni, Pb and Sb) in LHWF with concentration ranges from 0 to 500 ppm.



Four grams of the resulting paste is transferred to a single open-end sample cup which is sealed with a 4 µm thick Prolene® polypropylene film.

Calibration

For the calibration, a total of 24 samples were prepared. Each sample contains all six elements at different concentration levels spanning the concentration range of 0 to 500 ppm. This study opted for five concentration levels per element, combined according to uniform experimental design (24 calibration samples in total). Additionally, a blank and three samples with all elements at identical concentration levels (10, 250 and 500 ppm) were included in the calibrations.

An empirical calibration method using alpha coefficients to correct for matrix effects was used to perform the calibration. This method comes standard with the ARL QUANT'X quantitative software package and yields excellent results in virtually all applications, provided sufficient standards or calibration samples are available.

Calibration results

Figures 1 and 2 show the regression curves for Ni and Cd in LHWF. The plots demonstrate a good correlation between the element concentrations and the corrected intensities using the empirical calibration method. Table 2 shows the results obtained for all elements. The Standard Error of Estimate (SEE) is a measure of the difference between the given concentration and the measured concentration. A SEE of 5 ppm or less and correlation coefficients close to 1 demonstrate the excellent accuracy of this EDXRF method.

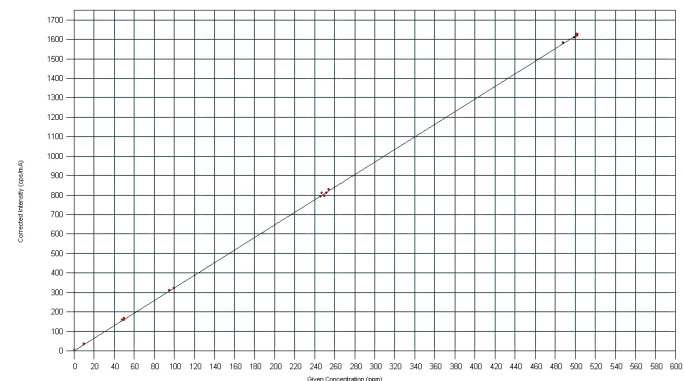


Figure 1. Regression curve for nickel in LHWF.

Excitation conditions

In EDXRF, sensitivity and precision are achieved by targeted excitation of the sample to fluoresce only the elements of interest. An instrument with more flexibility and control over the excitation efficiency and background typically shows better performance. The ARL QUANT'X offers a virtually unlimited combination of excitation voltages 4-50 kV and multiple primary beam filters for optimal background control. As shown in Table 1, three sets of conditions were used to collect three spectra per LHWF sample for a total counting time of twelve minutes. Whereas the analysis of liquids and sludge by XRF and other elemental techniques (ICP, AAS) is commonly carried out in an inert gas atmosphere such as helium, analyses for this study were conducted under ambient air avoiding significant consumable gas costs.

Table 1. Analytical settings.

Condition	Voltage (kV)	Tube filter	Medium	Counting time	Element
Mid Za	16	Pd Thin	Air	240	Cr, Ni
Mid Zc	28	Pd Thick	Air	240	Pb
High Zb	50	Cu Thick	Air	240	Ag, Cd, Sb

Sample preparation

All calibration standards were prepared according to ASTM D5839 using pure element oil standards (5,000 ppm) and paraffinic base oil. Before analysis, 5 g of the LHWF sample is thoroughly mixed with 5 g of graphite powder (mixing grade, 44 µm, 325 mesh) for five minutes using a ball mixer mill. Addition of graphite enables the homogenization of multi-phase liquids and decreases the variability in average Z. This approach minimizes matrix effects and ensures that a variety of LHWF samples can be analyzed with one calibration.

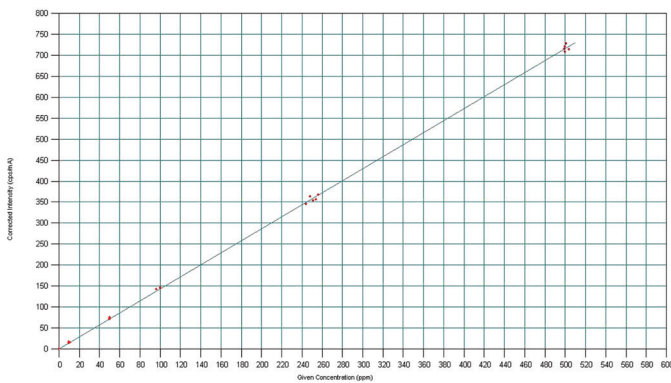


Figure 2. Regression curve for cadmium in LHWF.

Table 2. Calibration results.

Element	Conc. Range (ppm)	R ²	SEE (ppm)
Cr	0 – 500	0.9998	3
Ni	0 – 500	0.9999	2
Ag	0 – 500	0.9997	4
Cd	0 – 500	0.9998	3
Sb	0 – 500	0.9996	5
Pb	0 – 500	0.9998	3

Repeatability and detection limits

Repeatability tests were performed on a sample containing a nominal concentration of 250 ppm of each element. The sample was measured ten times in succession. Between measurements, the sample was removed from the instrument and then replaced. Measurement times identical to the calibration were applied. Table 3 shows the repeatability results and the minimum detection limits (MDL) based on peak and background intensities. Similar detection limits can be expected for neighboring elements as treated in ASTM D5839.

Table 3. Repeatability results and MDLs for a total analysis time per condition of four minutes. MDLs expected for an analysis time of only one minute per condition are also shown.

	Cr (ppm)	Ni (ppm)	Ag (ppm)	Cd (ppm)	Sb (ppm)	Pb (ppm)
1	253	251	260	253	261	259
2	255	250	261	258	265	267
3	254	252	258	261	267	263
4	250	251	261	260	266	268
5	254	251	261	266	267	267
6	249	251	261	259	269	269
7	254	251	264	263	266	269
8	254	253	260	263	267	269
9	257	252	260	265	263	270
10	258	250	259	260	268	268
Average	254	251	261	261	266	267
1-Sigma	2.7	0.8	1.6	4.0	2.3	3.4
MDL (240 s)	1.5	0.4	1.0	0.8	2.2	0.9
MDL (60 s)	3.0	0.7	2.0	1.7	4.4	1.8

Conclusion

The ARL QUANT'X EDXRF spectrometer with an SDD successfully quantifies trace elements in liquid hazardous waste fuels. Sample preparation using graphite as described in ASTM D5839 offers a fast and straightforward method to deal with the typical non-homogeneity of LHWF samples. A 60 second analysis time per condition under air yields detection limits of 5 ppm or less.

The speed, sensitivity, ease of use and reliability of the ARL QUANT'X make it an excellent analytical value for labs monitoring a wide range of liquid waste samples.

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