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ANALYSIS OF LIQUID HAZARDOUS WASTE USING THE ENERGO-DISPERZIVE X-RAY FLUORESCENCE SPECTROMETRY

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Abstract – Previously x-ray method was sometimes unable to accurately determine elements at low concentration in complex heterogeneous matrices. Other techniques can successfully use digestion and/or fusion methods to reduce samples to a dilute homogeneous form. However, when applying these methods of sample preparation to x-ray, detection limits were often unacceptable. The QuickSolve method is a simple but extremely effective manual operation that employs no expensive equipment. It requires a small plastic bottle preloaded with a fixed amount of the Environmental Sample preparation Matrix (ESPM). This is a totally safe, fine powder with high adsorption capacity. After adding a fixed mass of sample, manual shaking with stainless steel balls produces a stable principle for the analysis of complex matrices by x-ray, that is, dilution reduces all samples to similar form thus largely eliminating matrix and inter-element effects. The first group, acid producing elements, can be present at major concentrations, above one percent and acceptance of shipments may depend on the concentration of these elements. The QuickSolve calibration provides accurate determination of Br, Cl, I, P and S. Preparation of standards is from pure organic and aqueous solvent. The second group, heavy metals/toxic volatile elements, requires determination of some elements to better than 20 mg kg⁻¹. The calibration covers all relevant elements from vanadium to barium. Preparation of standards is from pure aqueous spectroscopic solutions. The analysis time is up to 15 minutes depending on the number of elements.

Keywords: x-ray fluorescence spectrometry

1. INTRODUCTION

A large proportion of hazardous industrial wastes are in liquid to semi-liquid forms and collectively they are known as liquid hazardous waste (LHW). Such wastes may be single phase liquid, multi-phase liquid and both of these with suspended solids. The management of LHW follows one of three routes:

- Recycling to produce a clean solvent or oil.
- Recovery of energy by use as an alternative fuel.
- Disposal by incineration at high temperature.

Re-cycling is becoming more common, especially with relatively well defined waste from automotive works, chemical plants and other industrial users of large quantities of solvents. Any residue from this recovery then goes through one of the two other routes. For use as an alternative fuel the LHW must be well characterised for acid producing elements (halogens, phosphorus and sulphur) and environmentally harmful elements. Only low concentrations of these components are acceptable to local regulatory bodies. High temperature incineration applies where the LHW contains high concentrations of any of the following: acid producing elements, toxic elements (such as heavy metals) and toxic volatile elements, that is cadmium, mercury, lead and thallium. All three of the above routes require analysis of the LHW.

The key purposes of these measurements are:

- To confirm the waste composition.
- To enable selection of the appropriate strategy for disposal.
- To ensure compliance with regulatory requirements.
- To ensure appropriate process control.

The elements fall into three groups of analytes:

1. Process control/acid generating elements
2. Heavy metals
3. Toxic/volatile elements

1.1. Process control/acid generating elements (Br, Cl, I, P, S)

These are necessary analytes for the effective control of the composition of combustion gasses. There must be control of the feed composition within the capacity of gas treatment facilities to ensure that emissions comply to limits. Where the manufacture of waste-derived fuel has a specification to ensure satisfactory performance then the confidence in the analysis must be high.

1.2. Heavy metals (Cr, Cu, Ni, V, Zn)

These are necessary analytes to ensure that performance meets regulatory requirements for releases to the environment, especially with limits for discharge to air and water. They are commonly occurring elements as wear metals in lubricating oils and impurities in fuel oils.

1.3. Toxic/volatile elements (As, Cd, Hg, Pb, Sb, Se, Sn, Tl)

These are important analytes because they are among the most hazardous and ever trace quantities can produce unacceptable atmospheric emissions. Their volatility causes them to evade many of the treatment stages that are effective for other heavy metals. Analytical techniques that involve ashing, heating or digestion are often unsuitable to determine these elements in LHW because this volatility causes losses during analysis. An incinerator operator must apply threshold levels for all process and regulatory controlled elements to ensure compliance. These levels vary from one installation to another depending on operational requirements.

2. THE QUICKSOLVE METHOD

2.1. Instrument Configuration

MDX-1080 X-ray Fluorescence Analyser
Rh standard window x-ray tube
Flexi channel for heavy metals
Monochromators for P, S, Cl
Helium system
XpertEase Windows software
Package ED01P

2.2. Accessories and Sample Preparation Equipment

Sample preparation equipment:

Powder sample cups
Poly-4 film, 4 μ m
Environmental Sample Preparation Matrix (ESPM) powder
Mixing balls
Sample mixing bottles
Tweezers
Accessories :
MES pellet
SUS60B and SUMI20B
8 position sample tray
Desiccator

2.3. The QuickSolve Method

Copying the Oxford Method D6052: All elements
Entering Oxford SUSs into the master standards database
Defining the parameters
Five Fixed Conditions - Elements, Atmosphere, Current, Livetime, Line, Units – for :
Very light elements
Liquids
Medium elements
Heavy elements traces
V. heavy elements

The light elements are determined using low kV conditions. The first row transition metals and Hg are measured using the Liquid and Medium elements conditions. Heavy elements from Mo-Ba are measured using the V. Heavy elements – traces conditions.

Any other elements – using the unexpected elements facility in QC limits.

Total Measuring time – 750 seconds – ensuring accurate results for low concentrations .

2.4. Calibration and Standardisation

Analytical standards – preparing gravimetrically by blending pure elemental standards – MBH Reference Materials

Concentration range – 0-600 mg kg⁻¹

2.5. Regression Setup

Restandardisation – Measuring Low and High Setting up Standards (SUS-s)

Low SUS – MES pellet

High SUSs – SUS60B and SUMI20B

Measuring instrument correction standards – automatically run peak position check standard (PPCS)

Measuring all the standards

Regression

Straight line calibrations for all elements

Background corrections.

2.6. Sample Preparation

Polyethylene bottle

15g+0.01g of ESPM

5g+0.01g of sample

Two 1 cm diameter stainless steel balls

Mixing.

Transferring sample into a standard 31.5 mm diameter vented sample cup fitted with Poly4 X-ray transmission film.

2.7. Analysis

Selecting a method and initialising analysis

Entering sample details

Placing the sample in the analysis position and starting analysis

3. PERFORMANCE

3.1. Accuracy

There are no certified reference standards of LHW to use for validation, and so it was necessary to employ the alternative technique of spiking and recovery. The base samples were two wastes from a high temperature incineration plant having low concentrations of the critical elements. They were a bi-phasal solutions that separated 30 seconds after mixing and a turbid solution containing particles that settled immediately after mixing. Separate portions of both samples had accurate amounts (spikes) of each element added after which the original and spiked samples were analysed. The difference between the two results for each element is the recovery and it should be the same as the additional or spiked amount.

Table 2 shows results with recoveries expressed as percentages of the spiked amounts. For the bi-phasal waste the average recovery is 104%. For the turbid waste (metals) it is 106% and 96% for acid forming elements. Therefore the average accuracy is 5% relative. That is equivalent to 2.5mg kg⁻¹ at 50mg kg⁻¹ and 5mg kg⁻¹ at 100 mg kg⁻¹.

Table 1: Standard errors for calibrations of the elements in LHW

Element	Units	Conc. range	Std error
P	%	0.1-5	0.13
S	%	0.05-5	0.056
Cl	%	0.05-5	0.066
Br	mg kg ⁻¹	10-10000	67
I	mg kg ⁻¹	10-2000	35
V	mg kg ⁻¹	5-600	6.1
Cr	mg kg ⁻¹	5-600	4.7
Mn	mg kg ⁻¹	0-1000	2.3
Fe	mg kg ⁻¹	5-4000	4.1
Co	mg kg ⁻¹	0-1000	3.9
Ni	mg kg ⁻¹	5-600	14.4
Cu	mg kg ⁻¹	5-600	11.8
Zn	mg kg ⁻¹	5-600	6.8
As	mg kg ⁻¹	5-600	4.4
Se	mg kg ⁻¹	5-600	5.3
Mo	mg kg ⁻¹	5-600	3.3
Rh	mg kg ⁻¹	5-600	1.0
Ag	mg kg ⁻¹	5-600	1.8
Cd	mg kg ⁻¹	5-600	1.9
Ba	mg kg ⁻¹	5-600	34
Sn	mg kg ⁻¹	5-600	2.5
Sb	mg kg ⁻¹	5-600	4.3
Hg	mg kg ⁻¹	5-600	4.6
Tl	mg kg ⁻¹	5-1000	7.8
Pb	mg kg ⁻¹	5-5000	13.1

Table 2: Validation of QuickSolve by spiking

Bi-phasal waste	Cd	Hg	Tl	Se	As	Pb
Spike conc. mgkg ⁻¹	47.1	101.8	102.5	104.6	109.7	183.7
Recovery %	108	103	98	109	109	99
Turbid waste	V	Cr	Fe	Ni	Cu	Zn
Spike conc. mgkg ⁻¹	103.3	102	106.4	104.5	103.5	106.6
Recovery %	102	110	104	118	94	105
Turbid waste	P	S	Cl	Br	I	
Spike conc. %m/m	0.849	0.805	0.858	0.042	0.845	
Recovery %	98	91	89	104	100	

3.2. Precision

To test the repeatability of the QuickSolve ten sample were prepared from one waste spiked with a metal (Cd) and another set spiked with an acid producing element (Cl). Table 3 shows the results.

Table 3: Repeatability

Element	Mean	Standard deviation	Relative standard deviation
Cl %m/m	1.45	0.027	1.9
Cd mg kg ⁻¹	56	1.3	2.2

3.3. Detection limit

Table 4 gives the Quicksolve detection limits for the main trace elements determined in LHW. Theoretical limits represent three standard deviations above the background signal.

Table 4: Detection limits

Element	Live time (secs)	Theoretical limit of detection (mg kg ⁻¹)	Guaranteed limit of detection (mg kg ⁻¹)
V	100	8	12
Cr	100	8	12
Fe	100	14	21
Ni	100	16	24
Cu	100	17	26
Zn	100	11	17
As	100	5	8
Se	100	5	8
Br	100	5	8
Mo	100	1	2
Rh	100	2.3	4
Ag	100	2.5	4
Cd	100	3	5
Sb	100	5	8
Sn	100	6	9
I	100	7	10
Ba	100	26	40
Hg	100	7	10
Tl	100	4	6
Pb	100	4	6

4. CONCLUSION

The key benefits of the QuickSolve method are:

1. Low on labour and material costs.
2. No potential analyte loss.
3. A single calibration applies to a wide range of matrix types.
4. Handles many sample forms, i.e. single phase, multi-phase and turbid liquids.
5. Calibration using easily obtained spectroscopic solutions and pure organic solvents.
6. Achieves a constant spectral background that makes matrix corrections unnecessary.
7. Dilution makes inter-element effects insignificant and therefore all calibrations are linear for the critical levels.
8. The prepared samples are safe to handle with no possible contamination of the spectrometer.
9. The sample mass (5g) is larger than for other techniques thus giving a more representative result.
10. Total time from receipt of a sample to the result is 15 to 30 minutes for 5 to 30 elements.
11. The method stabilises volatile samples and with the low power X-ray tube and heating loss during analysis is insignificant. High power system may still show losses.
12. The powerful combination of robust calibrations and stable instrumentation means there are no requirements for regular recalibration of the spectrometer. This reduces the number of quality assurance measurements needed to validate performance.

Table 5: A summary of the principle limitations of the analytical techniques currently in use for the analysis of LHW.

Technique	Elements	Sample Preparation	Key Limitations
Classical	Metals	Digestion, pH and buffering control, titration	Presence of unknown metals. Colour. Difficult to control pH.
Bomb Calorimetry	Halogens, P and S	Addition of reactive agents	Potentially determines only organic halides not total due to complexing of inorganic halides with metal species. Oxidation prevents determination of I.
ICP-AES, ICP-MS	Halogens, P, S and trace metals	Digestion	Halogen interference. Heating during preparation causes loss of important analytes e.g. Pb, Hg. Particulates. Large concentration of alkali metals can cause significant interference. Organic solvents.
AAS	Trace metals	Digestion	Halogens interference. Particulates. Organic solvents.
XRF	Halogens, P, S and trace metals	As received. Fusion. Digestion	Homogeneity. Loss of analytes in fusion or digestion process.

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