APPLICATION NOTE

Determination of hazardous elements in municipal solid waste with the ARL QUANT'X EDXRF Spectrometer

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Introduction

Municipal Solid Waste (MSW) is primarily produced by households. For a long time this waste has been deposited in municipal landfill sites. In recent years, MSW is regarded as a resource either by recycling certain fractions or through recovery operations such as conversion to energy and composting. MSW typically consists of plastics, textile, cardboard/paper and organic matter. Chemical characterization of waste to determine any hazardous elements is critical to determine the processing route. In addition, when incineration is considered, any corrosive elements (S and Cl) as well as ash forming elements are of interest as well. Energy-Dispersive X-Ray Fluorescence (EDXRF) is a cost-efficient instrumental technique to determine all elements of interest at concentrations of a few ppm to % w/w.

Instrumentation

The Thermo Scientific™ ARL QUANT'X™ XRF Spectrometer is an EDXRF system providing a fast and cost-effective analytical capability. It is fitted with an air-cooled Rh end-window tube with thin Be window (0.05 mm) and has a maximum power of 50 Watts. The ARL QUANT'X Spectrometer is equipped with an electrically cooled silicon drift detector (SDD) with an area of 30 mm^2. The instrument features a total of nine primary beam filters ensuring that an optimal excitation condition is always found. An optional 10-position sample changer allows for unattended analysis.

Sampling and sample preparation

Being an inhomogeneous material the composition of MSW varies significantly and sampling remains the biggest source of error. Preparing the sample for XRF analysis is equally important to obtain reliable results. To obtain a homogenous sample the sample is ground using a cutting mill resulting in a particle fineness of 0.25-4.0 mm. A particle size of 500 microns or less is sufficient for the determination of medium to heavy elements. Lighter elements might require further grinding – down to 50 micron – by means of a rotor mill. After grinding the sample is mixed with a binding agent and pressed into a pellet.

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Quantitative method

When a representative suite of standards is available, excellent results can be obtained using an empirical calibration relating characteristic peak intensity to concentration possibly combined with Compton correction to adjust for variances of the sample matrix. Depending on the diversity of the waste received, a set of well characterized standards is often hard to obtain. With the Thermo Scientific™ UniQuant™ Software for EDXRF, our proprietary standard-less FP-based software, good quantitative results are obtained while only a few standards are required to set up the calibration.

Excitation conditions

In EDXRF, sensitivity and precision are achieved by targeted excitation of the sample to fluoresce only the elements of interest. The ARL QUANT'X EDXRF Spectrometer offers a wide range of excitation voltages (4-50 kV) and multiple primary beam filters for optimal background control.

As shown in Table 1, eight spectra are collected per waste sample for a total live time of 7 minutes, corresponding to less than 15 minutes real time per sample (including detector dead time).

Table 1: Excitation Conditions

Voltage (kV)	Tube Filter	Atmosphere	Live Time (s)	Elements of Interest
4	No Filter	Vacuum	60	Na, Mg, Al, Si
8	C Thick	Vacuum	30	S, Cl
12	Al	Vacuum	60	V, Cr
16	Pd Thin	Vacuum	30	Fe, Co
20	Pd Medium	Vacuum	60	Ni, Cu, Zn
30	Pd Thick	Vacuum	60	As, Br, Hg, Pb
50	Cu Thin	Vacuum	60	Mo, Cd
50	Cu Thick	Vacuum	60	Sn, Sb, Ba

Calibration and validation

When the type of MSW being analyzed is well characterized and expected to consist of a mixture of plastics, textile, paper and organic matter, UniQuant Software is easily calibrated using a set of polymer and cellulose standards. For this application we have used different polymer standards as well as cellulose samples doped with heavy elements at different concentrations.

To validate the method several MSW samples have been analyzed using both the ARL QUANT'X Spectrometer combined with UniQuant Software as well as ICP-OES. Samples of MSW were ground down using a Retsch SM200 cutting mill (500 micron particle size). The resulting powder was divided into two parts. One part was used to press samples using a wax binding agent and analyzed with the ARL QUANT'X Spectrometer. The remaining part was used to be analyzed with ICP-OES. Sample preparation for the ICP-OES consisted of digestion using a HF:HNO_3:HCl solution. Table 2 compares the results found for one of the MSW samples. The relative difference is shown to be less than 30% for all elements. It can be concluded that a good agreement between ICP and EDXRF results is achievable.

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Method detection limits

Table 3 shows the Method Detection Limits (MDLs) that can be expected for the ARL QUANT'X EDXRF Spectrometer.

Table 2: Analysis results for a typical MSW sample, obtained by EDXRF and ICP-OES . Excellent agreement is found considering the type of material that was analyzed.

Element	ARL QUANT'X + UQED (% w/w)	ICP-OES (% w/w)	Relative Difference (%)
Al	1.02	1.08	6.7
Ba	0.108	0.131	20.9
Br	0.0026	-	-
Ca	4.30	4.45	3.5
Cl	0.655	-	-
Cr	0.054	0.043	-21.2
Cu	0.083	0.085	1.7
Fe	1.20	0.94	-21.7
K	0.073	0.077	5.4
Mn	0.030	0.029	-3.1
Ni	0.012	0.009	-26.8
P	0.092	0.108	17.8
Pb	0.030	0.022	-28.2
Sb	0.0021	0.0019	-10.3
Si	1.30	-	-
Sn	0.0108	0.0099	-8.3
Sr	0.0056	0.0063	13.3
S	0.748	0.712	-4.7
Ti	0.416	0.302	-27.3
Zn	0.256	0.272	6.4

Although MDLs might vary depending on the matrix and elements present, table 2 shows that the MDLs allow for a quick screening of MSW to identify any hazardous elements.

Table 3: Typical Method Detection Limits (MDL) obtainable for the ARL QUANT'X Spectrometer when analyzing MSW samples

Element	S	Cl	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
MDL (ppm)	45	60	6	6	6	3	3	2	2	2
Element	**As**	**Se**	**Br**	**Mo**	**Cd**	**Sn**	**Sb**	**Ba**	**Hg**	**Pb**
MDL (ppm)	3	3	3	4	5	6	12	50	5	4

Conclusion

This application note illustrates the feasibility to use the ARL QUANT'X EDXRF Spectrometer as a cost-efficient solution to screen Municipal Solid Waste (MSW) samples for the presence of any hazardous elements. While the sample preparation is kept to a minimum, the technique allows for the detection of all elements of interest.

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