



TXRF

Analysis of Mercury Traces in Glass by TXRF Spectrometry

Application Note # XRF 424

Introduction

The usage of mercury is essential in the lighting industry, although it is known as a hazardous element. With regard to recycling and production processes, the accurate control of maximum contamination levels of this element is of crucial importance. Due to mercury's high volatility at room temperature, trace analysis of the element is complicated. Common methods like Cold Vapor Atomic Absorption Spectroscopy (CV AAS) are very time consuming and cost intensive. In this study, the capability of the S2 PICOFOX TXRF spectrometer for the determination of low mercury concentrations is demonstrated by the analysis of a reference glass standard.

Parameter	Specifications
Tube	Air-cooled metal ceramic Mo-anode Max. power 50 W
Optics	Ni/C - Monochromator (17.5 keV)
Detector	Si drift detector XFlash® Area: 10 mm ² FWHM: < 160 eV (Mn Ka)☒
Size (DxWxH)	450 x 590 x 300 mm
Weight	37 kg

Table 1

Technical parameters of the TXRF spectrometer S2 PICOFOX

Analysis and sample preparation

All analyses were performed using a S2 PICOFOX TXRF spectrometer. A summary of the technical parameters of the instrument is shown in Table 1.

First, the glass powder was analysed qualitatively. With a Q-tip a small quantity of the sample was transferred directly to a sample carrier made of quartz glass. The measurement time was set to 1000 seconds. The goal of this fast screening was to get information about the element content of the glass sample, especially for the selection of an internal standard.

Due to the absence of this element in the glass spectrum (Figure 1) selenium was used as an internal standard for the quantification. For quantitative analysis, the sample material was prepared as a suspension. 800 mg of the glass powder were mixed with 10 ml of a 1% Triton X100® solution. After addition of 10 µl Se standard solution (1 g/L) the suspension was thoroughly homogenized. 5 µl of this suspension have been transferred onto a quartz glass sample carrier and dried in a desiccator. Two homogenized suspensions were measured in triplicate for 1000 seconds each.

Results

The mercury content of the glass sample was certified by external laboratories using CV AAS according to the method published by the ICG/TC 2. The results are listed in Table 2. The element content of the glass, including additional elements measured simultaneously, estimated by the S2 PICOFOX is shown in Table 3.

Additionally the limit of detection (LOD) for Hg was calculated to a value of 0.20 mg/kg using the following equation (Klockenkämper, 1997).

$$LOD = 3 \cdot \frac{c}{I_{net}} \cdot \sqrt{(2 \cdot I_{bg})}$$

c: element concentration

I_{net} : net intensity

I_{bg} : background intensity

Analysis	Hg (mg/kg)	Std. dev. (mg/kg)
1	2.8	0.3 (n=10)
2	2.9	0.3 (n=7)
3	2.13	n.d.
4	2.19	n.d.
5	2.42	n.d.
6	2.5	0.07 (n=6)

Table 2

External measurement results for the Hg glass sample (CV AAS analysis)

Element	Hg glass (mg/kg)	Std. dev. (mg/kg)	LOD (mg/kg)
S	12.9	3.3	8.1
Cl	32.4	2.2	5.2
K	1865	287.6	5.3
Ca	8481	1349.5	7.2
Ti	66.8	9.5	1.6
Cr	4.0	1.1	0.66
Mn	8.7	2.2	0.54
Fe	281.0	75.7	0.58
Ni	0.50	0.2	0.26
Cu	2.6	0.8	0.22
Zn	2.3	0.4	0.18
Ga	0.78	0.6	0.15
As	4.7	2.9	0.14
Rb	14.4	4.6	0.24
Sr	50.1	14.6	0.28
Y	16.2	4.6	0.43
Ba	930.4	198.3	3.1
Hg	2.2	0.3	0.20
Pb	12.6	3.5	0.22

Table 3

External measurement results for the Hg glass sample (CV AAS analysis)
No. of measurements = 6

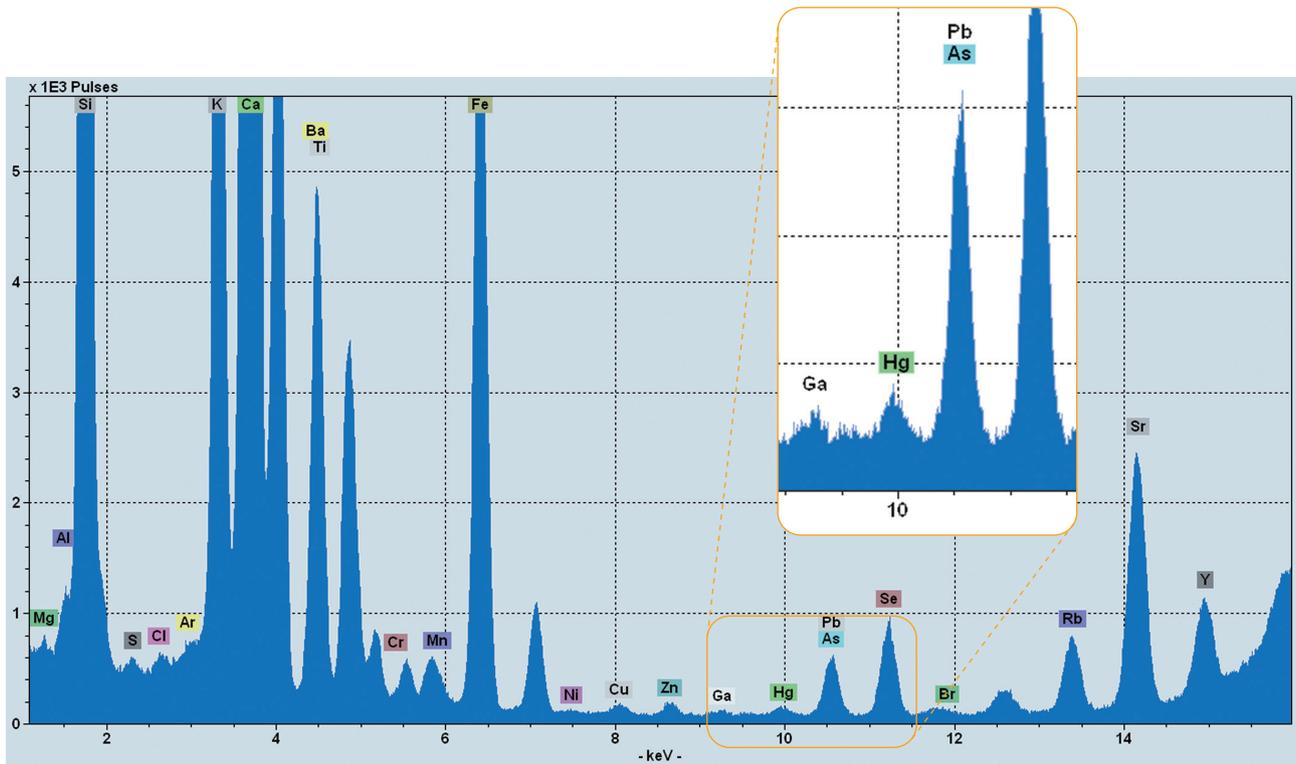


Figure 1
Spectrum of a Hg glass powder Recycling glass with 2.5 mg/kg Hg, measurement time 1000 s

Comparison of CV AAS and TXRF

	CV-AAS	TXRF (S2 PICOFOX)
Sample preparation	High-temperature digestion	Suspension, internal standardisation, drying on sample carrier
Reagents	Nitric, Perchloric, Hydrofluoric and Hydrochloric Acid Mercury (II) Chloride Sodium Borohydride/Sodium Hydroxide Tin (II) Chloride Grade 2 Water	Triton X100 solution Grade 2 Water
Preparation time	> 1 hour	~ 10 minutes
Calibration	4 calibration solutions + 1 blank solution	Internal standardization
Measurement time	~ 180 seconds/element	~ 1000 seconds
Remarks	Mono-element method Memory effects may occur when analysing high - concentrated (> 0.015 µg/l) solutions	Multi-element method

Table 4
Reproducibility of TXRF measurements of drugs, sample „Aspirin, no name, USA“, average of 10 measurements

Conclusion

The measurement results show that the S2 PICOFOX TXRF spectrometer is suitable for the analysis of low mercury concentrations in glass samples.

The detection limit is one order of magnitude lower than the actual value, which clearly demonstrates the suitability of TXRF. In Table 4 both analytical techniques, TXRF and CV AAS, are compared with regard to the Hg-analysis in glass. A major benefit of the TXRF - technique is that sample preparation is very fast, uncomplicated and can be done without the usage of acids. In addition, no solutions for external calibration have to be prepared, because TXRF works by means of internal calibration.

Additional benefits of the TXRF method are the possibility of multi-element analysis and the avoidance of memory effects mentioned in the ICG/TC 2/99.

Literature

Klockenkämper, R. (1997): Total-Reflection X-Ray Fluorescence Analysis, Wiley & Sons.

International Commission on Glass, Technical Committee 2 (1999): Determination of mercury in glass by Cold Vapour Atomic Absorption Spectrometry (CV AAS), ICG/TC 2/99-1194.

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