



TXRF

Analysis of Mercury in Tap Water and Orange Juice by TXRF Spectrometry

Application Note # XRF 430

Introduction

Mercury is released in the environment by natural sources (volcanoes) and industrial activities (coal-fired power plants, gold production, cement and non-ferrous metal industry). Therefore, Hg (II) is still a frequent component of drinking water sources, waste water and agricultural products.

Due to the toxicity of this element the World Health Organisation (WHO) recently published a recommendation for the maximum input of 2 $\mu\text{g}/\text{kg}$ of body weight per day (TDI) [1]. Regarding to drinking water the maximum contamination levels (MCL) for Hg in drinking water are set to 1 $\mu\text{g}/\text{l}$ according to european regulations (directive 98/83) or to 2 $\mu\text{g}/\text{l}$ according to the US-EPA (Safe Drinking Water Act, 1974).

Based on these low threshold values any analytical approach for Hg analysis requires extremely sensitive instrumentation. Today, most common methods are cold vapor atomic adsorption spectroscopy (CV-AAS) and inductively coupled plasma mass spectroscopy (ICP-MS). CV-AAS offers detection limits below 0.1 $\mu\text{g}/\text{l}$ for Hg, but is restricted

to the analysis of this element only. Even better sensitivities including the capability for multi-element analysis can be achieved by ICP-MS. The major disadvantage is the sophisticated use of this technology and continuous high operation costs.



When samples are applied for Total Reflection X-Ray Fluorescence (TXRF) analysis without further treatment, the analysis of Hg (II) is not possible, because a significant amount of this volatile element is lost through evaporation during sample preparation.

In this paper the results for Hg (II) analysis, applying a sample preparation technique according to recently published data [2], are presented.

Instrumentation

All measurements were performed using the bench top TXRF spectrometer S2 PICOFOX. This instrument is equipped with an air-cooled low power X-ray tube (Mo target), a multilayer monochromator with 80% reflectivity and the liquid nitrogen-free XFlash® Silicon Drift Detector (SDD) with an energy resolution of < 159 eV (Mn K α).

Sample preparation and measurements

Samples analyzed were drinking water from the tap and commercially obtained orange juice. The samples were spiked with a Hg mono-element standard solution (Merck 1 g/l) in order to obtain concentrations ranging from 50 to 500 $\mu\text{g/l}$. Complexation of the Hg (II) was performed by addition of a concentrated aqueous solution of ethylenediaminetetraacetic acid (EDTA, Figure 1) in a ratio of 1:3.

After thorough homogenization 10 μl of the sample solution was transferred to a clean quartz glass sample carrier and dried in a desiccator.

All samples were prepared as duplicates and analyzed with a measurement time of 1000 s or 3600 s, respectively.

Results

The results of the measurements are summarized in Table 1, a graphical comparison of the nominal spike values and the TXRF results is given in Figure 2.

Obviously, a systematic underestimation of Hg occurs, if no EDTA is added to the samples prior to the preparation steps. This clearly

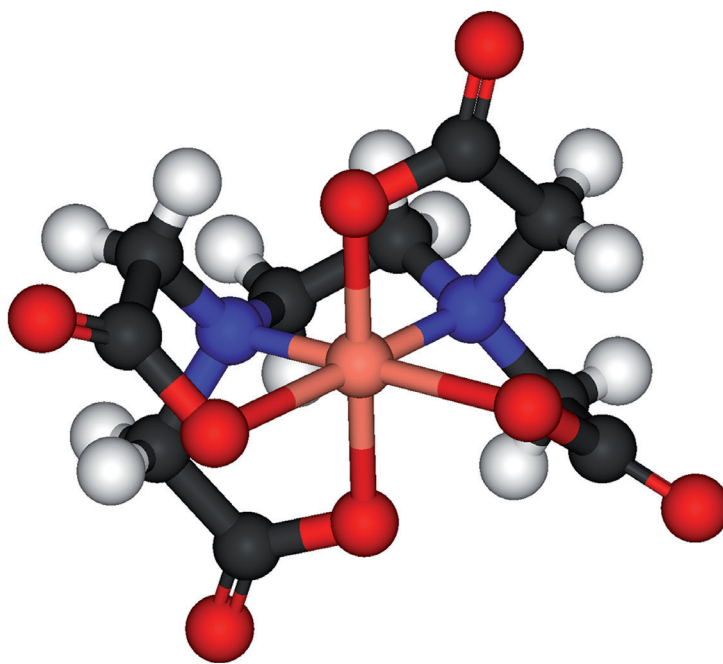


Figure 1
An EDTA molecule coordinating a Metall²⁺ ion

Spike	Tap water (- EDTA)	Tap water (+ EDTA)	Orange juice
500	439 \pm 3.3	542 \pm 3.2	511 \pm 7.9
250	123 \pm 1.3	272 \pm 2.0	245 \pm 6.1
100	39 \pm 0.7	96 \pm 1.5	89 \pm 4.5
50	22 \pm 0.6	48 \pm 0.9	41 \pm 4.5

Table 1
Quantitative TXRF results of tap water and orange juice spiked with different mercury concentrations. All concentrations in $\mu\text{g/l}$.

	Tap water (1000 s)	Tap water (3600 s)	Orange juice (1000 s)
LOD ($\mu\text{g/l}$)	1.20	0.58	7.90

Table 2
Calculated detection limits for mercury in tap water and orange juice

demonstrates the loss of the volatile Hg during the drying process. Samples treated with EDTA show a good concordance of the measured data and the expected spike values.

The limits of detection (LOD) listed in Table 2 were calculated with the following formula [3]:

$$LOD(\mu\text{g/l}) = 3 \cdot \frac{c(\mu\text{g/l})}{I_{\text{net}}(\text{counts})} \cdot \sqrt{2 \cdot I_{\text{bg}}(\text{counts})}$$

LOD: Limit of detection ($\mu\text{g/l}$)

c: Element concentration ($\mu\text{g/l}$)

I_{net} : Net intensity (counts)

I_{bg} : Background intensity (counts)

The high matrix content of orange juice leads to a much higher scattering background, which inevitably results in higher detection limits. Similar detection limits in the range of 10 $\mu\text{g/l}$ can be expected for samples with comparable matrix content like wine, blood, urine and other biological samples.

For tap water the LOD value for Hg is close to the required threshold values. To be on the safe side and to reach detection limits in the sub-ppb range longer measurement times are strictly recommended (3600 s in this report).

Finally, the addition of EDTA has almost no impact on the detection limits for Hg in tap water (Figure 3).

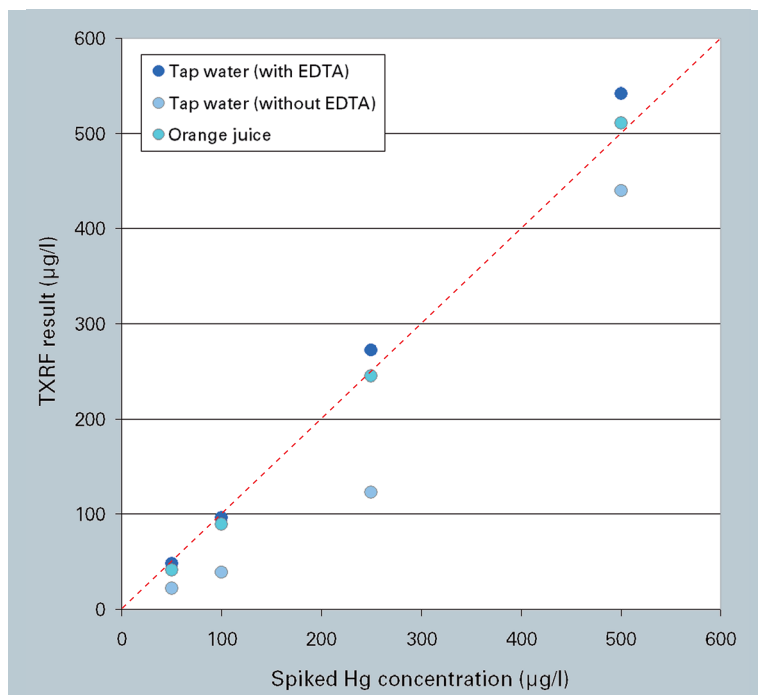


Figure 2

Comparison of spiked and measured mercury values in tap water and orange juice

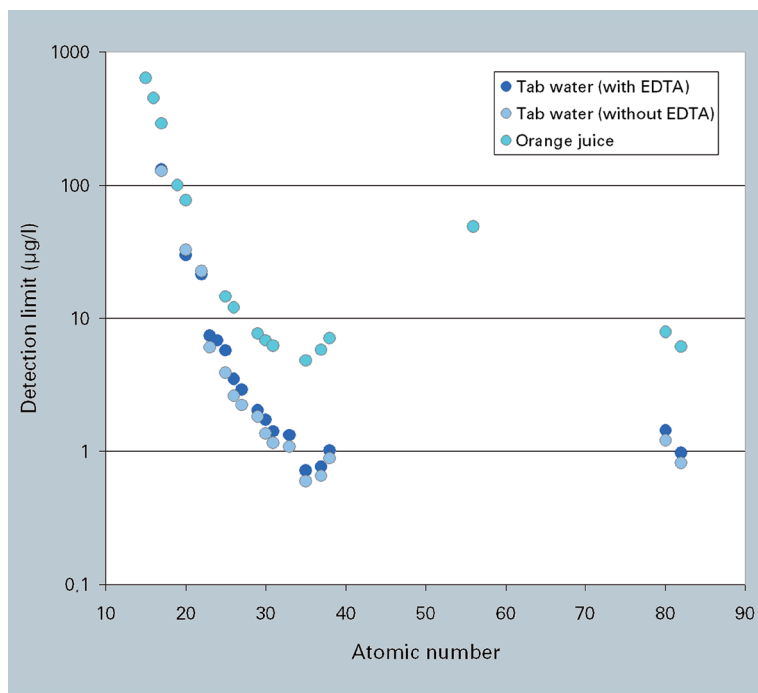


Figure 3

Detection limits (measurement time 1000 s) for different elements in tap water and orange juice

Conclusion

The data presented in this paper clearly demonstrate the applicability of TXRF for the analysis of mercury in water samples and liquid biological matrices.

Common methods like CV-AAS and ICP-MS are extremely sensitive for liquid samples. But these analytical methods require time-consuming and costly sample preparation steps, which often include the use of hazardous chemicals. Therefore, a low-power bench top TXRF spectrometer must be considered as an ideal supplementary tool for the detection of low mercury concentrations.

Literature

- [1] Mercury in drinking water, WHO 2005, http://www.who.int/water_sanitation_health/dwq/chemicals/mercuryfinal.pdf
- [2] Custo, G. et al.: Total reflection X-ray fluorescence trace mercury determination by trapping complexation: Application in advanced oxidation technologies, Spectrochim. Acta Part B 61 (2006), 1119-1123
- [3] Klockenkämper, R. (1997): Total-Reflection X-Ray Fluorescence Analysis, Wiley & Sons.

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