

Environmental applications of Horizon TXRF spectrometer

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1. Foreword

TXRF is a type of Energy Dispersive X-Ray Fluorescence (EDXRF) in which the X-Ray beam strikes the sample, deposited as a thin layer on a carrier, at a very small incidence angle, in order to exploit the excitation enhancement given by the total reflection effect. As far as the sample is thin enough (thin film approximation), the technique's main strengths are:

- no matrix effect;
- no matrix dependent calibration curves;
- improved detection limits (LOD);
- simultaneous multi-element analysis;
- minimum amount of sample;
- microanalysis capabilities.

The sample should be deposited in liquid/slurry form onto the carrier (reflector) and then dried, in order to leave only a thin residue film. If the sample is in powder form, it must be dissolved or transferred into a suspension. Whatever the sample, quantitative analysis can be performed by adding an internal standard, i.e. an element which is not present in the original sample (usually Ga, Sc or Co)¹.

Depending on the sample, analysis can be carried out on the "as is" specimen or after a treatment step, e.g. dilution, digestion, ashing, on-site enrichment etc. In many cases, the correct sample preparation is instrumental in getting low LOD and accurate quantification.

In the following lines, some results obtained with the Horizon benchtop instrument will be reported. Read reference publications^{2 3} for further examples and details.

¹ ISO/TS 18507:2015(E); R. Klockenkämper A. von Bohlen, Total-Reflection X-Ray Fluorescence Analysis and Related Methods, John Wiley & Sons, Inc., DOI:10.1002/9781118985953,

² D. Monticelli, A. Cinosi, G. Siviero, L. Seralessandri, Trace element determination in soy sauce: A novel total reflection X-ray fluorescence procedure and comparison with inductively coupled plasma-mass spectrometry, Spectrochimica Acta Part B: Atomic Spectroscopy, Volume 146, 2018, Pages 16-20, <https://doi.org/10.1016/j.sab.2018.04.022>

³G. Siviero, A. Cinosi, D. Monticelli, L. Seralessandri, Determination of trace metals in spirits by total reflection X-ray fluorescence spectrometry, Spectrochimica Acta Part B: Atomic Spectroscopy, Volume 144, 2018, Pages 15-19, <https://doi.org/10.1016/j.sab.2018.03.006>.

2. Instrument Set Up

Technique:	TXRF
Spectrometer:	Horizon
Source:	Fine Focus Mo anode, line
Voltage [kV]:	40
Current [mA]:	15
Monochromator:	W/Si multilayer
Excitation:	Mo Ka
Sample carrier (x 12):	Quartz reflector
Detector type:	Ketek AXAS D SDD (20 mm ²) with graphene window



3. Water samples

An artificial water sample at 10 $\mu\text{g}/\text{kg}$ level was made by diluting a MES ICP IV solution at 1000 mg/l with ultrapure water (18.2 M Ω .cm). Gallium, already present in the solution, was used as internal standard. 8 μl were pipetted onto a siliconized quartz reflector and then dried on a hot plate at 80° C. On-site enrichment was performed by repeating the deposition several times on the same reflector, in order to reduce the LODs (Fig. 1 and 2). See Cinosi et al.⁴

Spectra for blank reflectors were collected too. The best LOD with good recovery values ($\pm 10\%$) were obtained above 200 μl and integration time of 1000 s (Fig. 3).

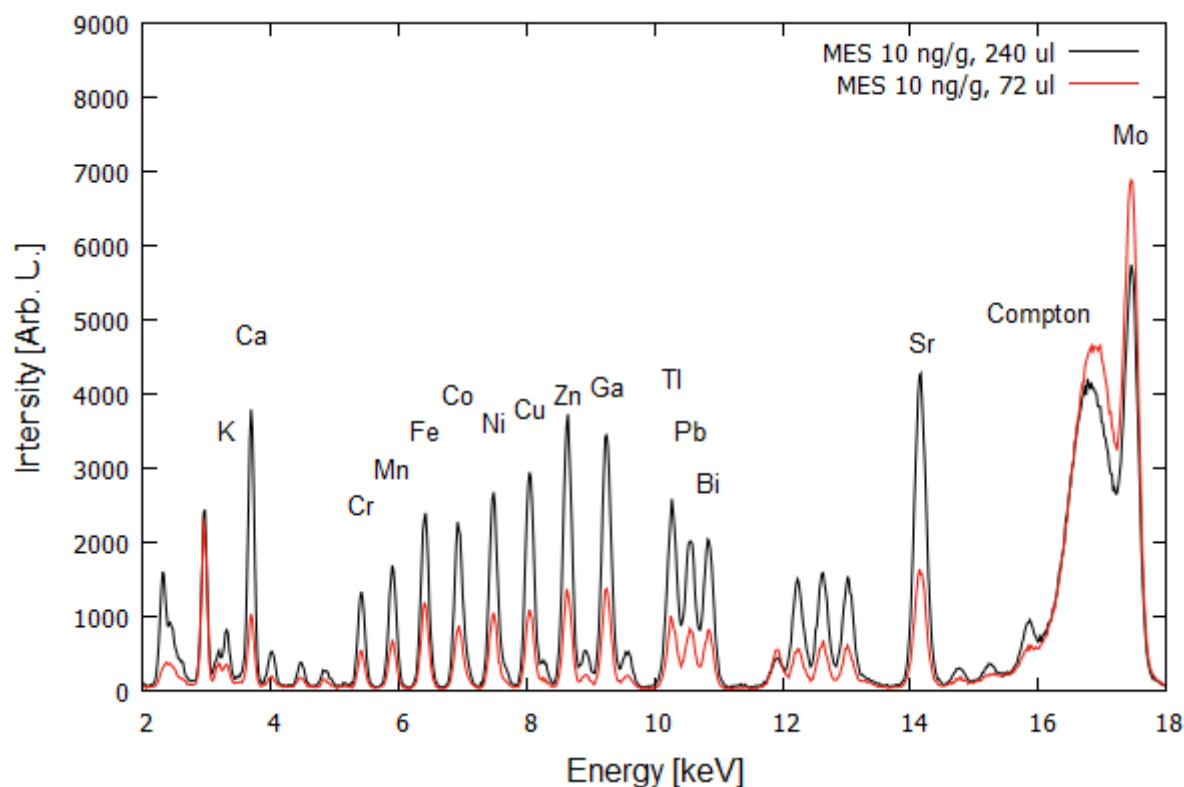


Fig.1. Example of spectra for water sample at different enrichment level but same integration time.

⁴ Cinosi, A., Andriollo, N., Pepponi, G. et al. Anal Bioanal Chem (2011) 399: 927. <https://doi.org/10.1007/s00216-010-4352-x>

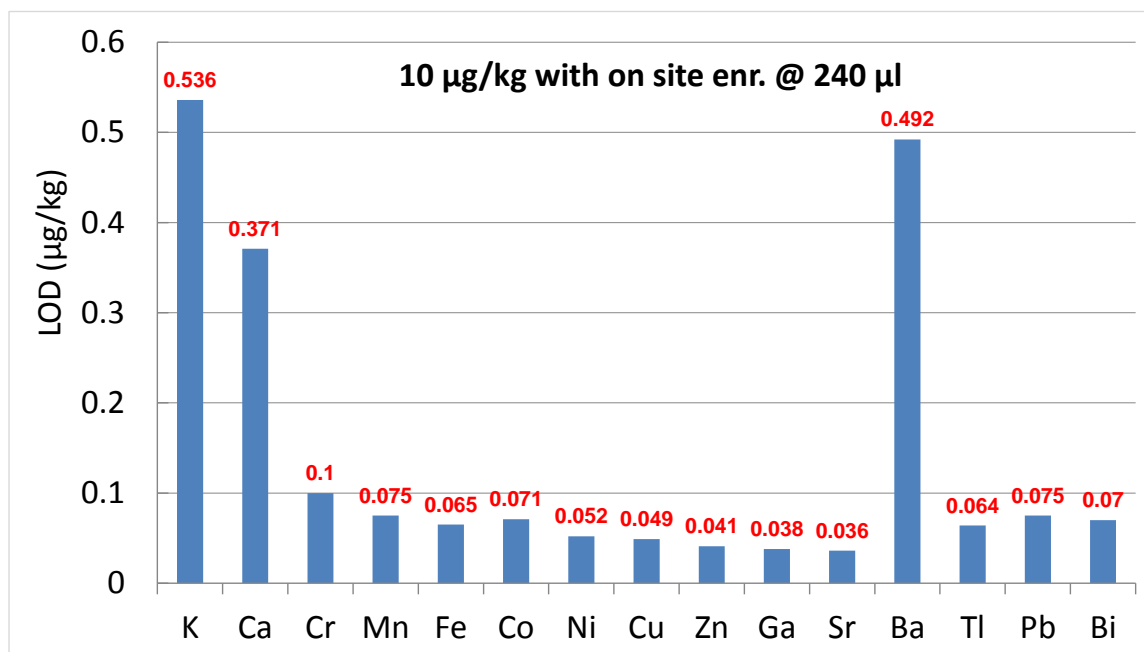


Fig.2. Limit of detection for analytes at 240 µl (enrichment=30).

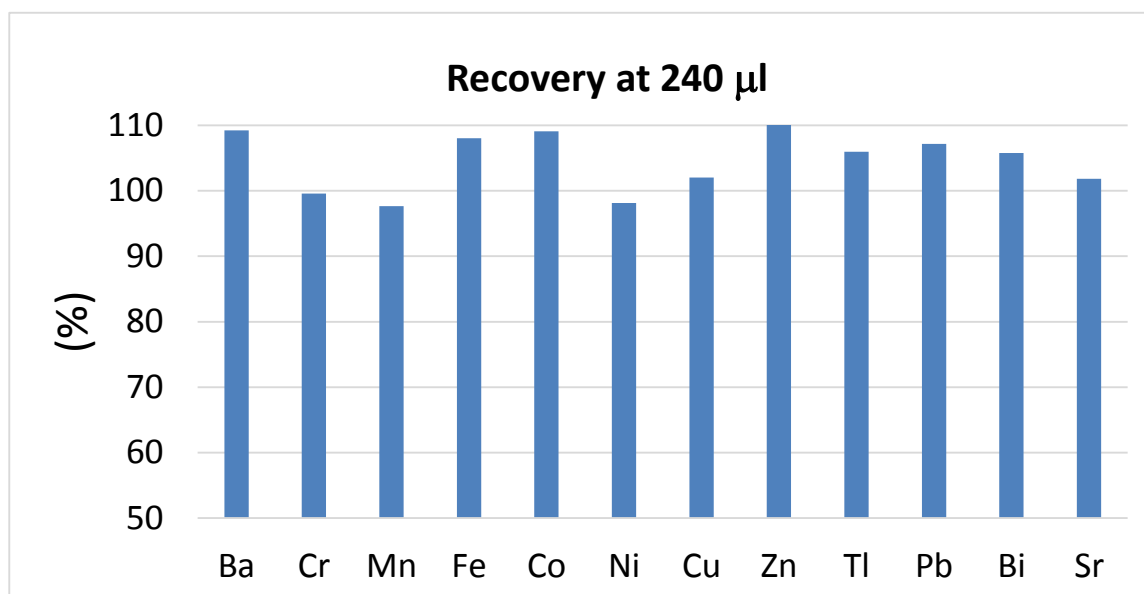


Fig.3. Recovery values at 240 µl.

After assessing the instrument detection capabilities with a fictitious sample, a real tap water specimen was analyzed in triplicate. Gallium internal standard was added with a concentration of 161 $\mu\text{g}/\text{kg}$. It is expected that on-site enrichment is less effective and LODs are larger in this case, due to the larger amount of Na, Mg and Ca. If it was sea water, the situation would be even worse. Results for 40 μl are reported in Table 1, including As. LOD values are reported in Fig. 4: it is apparent that values are larger with respect to the fictitious sample, but still below 1 $\mu\text{g}/\text{kg}$ for transition metals. A standard procedure for water analysis by means of TXRF has become recently available⁵: taking into account the results shown above, the Horizon spectrometer fits it well.

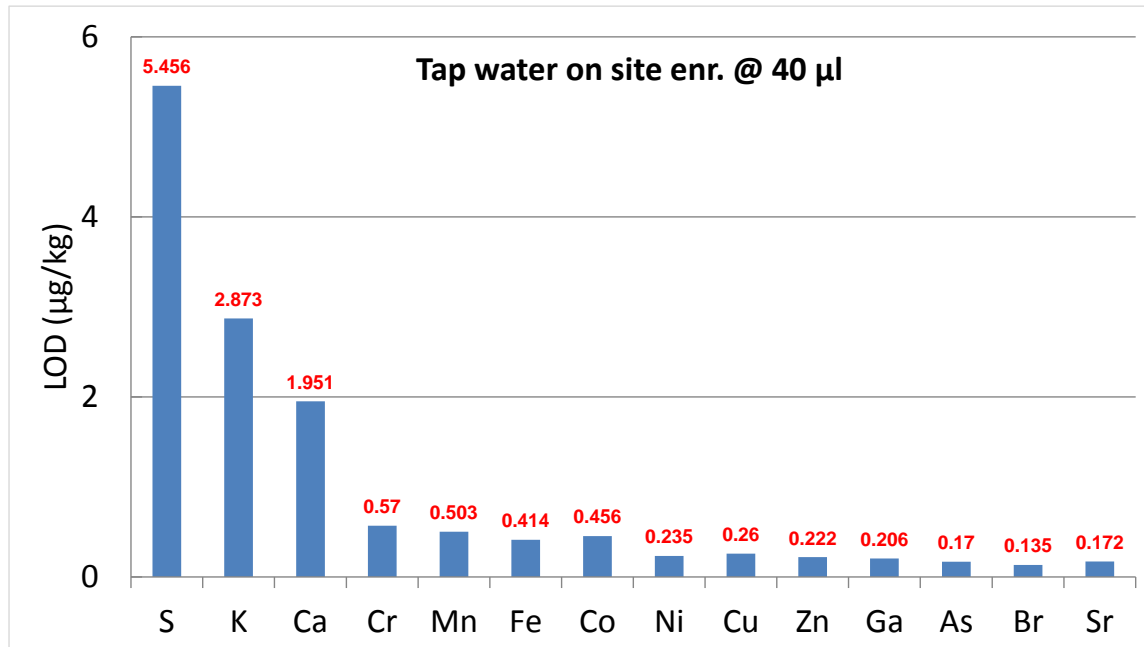


Fig.4. Limit of detection for tap water 40 μl (enrichment=5).

⁵ ISO 20289:2018 Surface chemical analysis -- Total reflection X-ray fluorescence analysis of water

Table 1. Results for tap water.

	Average ($\mu\text{g}/\text{kg}$)	SD ($\mu\text{g}/\text{kg}$)	RSD (%)
S	1400.5	117.0	8.4
K	613.7	3.2	0.5
Ca	5168.9	59.5	1.2
Cr	1.6	0.6	38.3
Mn	2.7	0.6	21.5
Fe	83.8	0.2	0.3
Ni	0.4	0.1	19.5
Cu	2.7	0.1	4.6
Zn	10.6	0.3	2.5
Pb	0.9	0.1	13.2
As	3.8	0.1	3.7
Br	2.6	0.4	15.6
Sr	22.7	0.3	1.4

4. Tobacco leaves

Tobacco naturally accumulates and concentrates relatively high levels of heavy metals in leaves: thus, its analysis is important both for environmental pollution assessment and consumer safety. CTA OTL-1 standard consists of dried, ground and sieved tobacco leaves. The powder was put into ultrapure water (18.2 MΩ.cm) with a suitable solvent to increase the particle wettability and reduce the sedimentation rate. After deposition on a quartz reflector, the sample was measured in triplicate both “as is” and after treatment at 120° C in HNO₃ vapour atmosphere, i.e. Atmospheric Pressure Vapor Phase Decomposition (AP-VPD), in order to remove the organic matrix. For details see Cinosi et al.⁶ and reference 3. The integration time was 600 s per specimen.

Results are reported in Table 2 and Fig. 5: on the one hand VPD allows to slightly improve LOD values, on the other hand it involves the loss of Cl and Br. Recovery values for both methods are good and compliant with the Codex Alimentarius guidelines⁷.

It must be pointed out that for this kind of samples the particle size should be small enough (e.g. <70 μm) in order to be representative, so appropriate drying, grinding and sieving procedures should be carried out. See R. Dybczyhski et al.⁸.

⁶ Amedeo Cinosi, Nunzio Andriollo, Francesca Tibaldi, Damiano Monticelli, Atmospheric pressure vapour phase decomposition: A proof of principle, *Talanta*, Volume 101, 2012, Pages 148-150, <https://doi.org/10.1016/j.talanta.2012.09.029>.

⁷ Codex Alimentarius Commission (FAO-WHO), Procedural Manual, 24th edition

⁸ <https://inis.iaea.org/collection/NCLCollectionStore/Public/28/066/28066591.pdf>

Table 2. Results for OTL-1 with two different preparation methods. Both relative standard deviation (RSD) and accuracy (as RE) are reported.

[ppm]	Ref. data	As received					VPD				
		Average	Std. Dev.	LOD	RSD[%]	RE[%]	Average	Std. Dev.	LOD	RSD[%]	RE[%]
S	7320	6537	33	207	0.5	-11	6377	636	180	10.0	-13
Cl	298	259	13	129	4.9	-13			20		
K	15600	13707	8	47	0.1	-12	15058	1078	43	7.2	-3
Ca	31700	31416	108	27	0.3	-1	31612	568	7	1.8	0
V	3.08	<5		5			<4		3.9		
Cr	2.59	<5		4.7			<3		3.2		
Mn	412	397.9	1.2	3.3	0.3	-3	397.7	16.8	3.0	4.2	-3
Fe	989	832.9	125.7	2.3	15.1	-16	944.0	117.0	2.3	12.4	-5
Ni	6.32	6.1	1.0	1.9	16.2	-4	4.4	0.9	1.5	21.7	-31
Cu	14.1	13.1	3.1	1.7	23.5	-7	16.1	0.4	0.9	2.7	14
Zn	49.9	48.1	1.7	1.6	3.5	-4	48.8	3.1	0.7	6.3	-2
As	0.5	<0.9	0.1	0.95			<0.6		0.6		
Br	9.28	10.1	1.3	0.82	12.7	8	<0.6		0.6		
Rb	9.79	8.2	0.04	0.85	0.5	-16	8.1	0.1	0.6	0.9	-18
Sr	201	217.3	0.4	0.86	0.2	8	210.5	0.7	0.7	0.3	5
Ba	84.2	85.1	2.1	19	2.4	1	56.0	7.1	14.6	12.7	-33
Pb	4.91	3.9	1.0	3	26.0	-21	4.0	0.4	1.4	8.8	-19

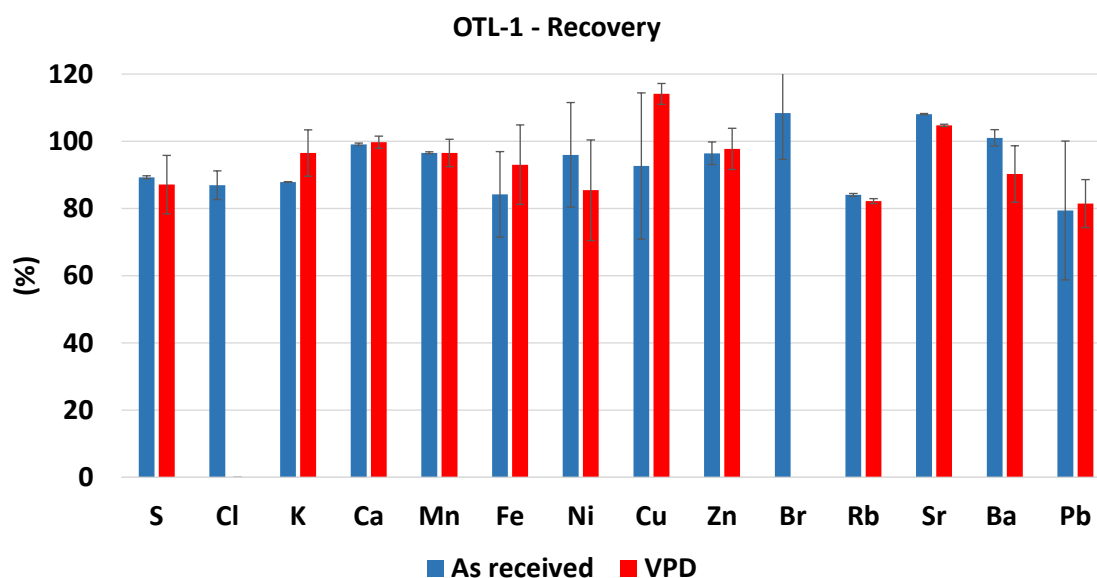


Fig.5. Recovery values for Tobacco leaves OTL-1 with two different sample preparation methods.

5. Domestic sludge

NIST 2781 domestic sludge was ground by a Retsch MM 400 vibratory mill equipped with zirconia jars and balls.

After weighing, the sample was suspended in a 2% HNO₃ solution of ultrapure water (18.2 MΩ.cm) and N-Methyl-2-pyrrolidone (NMP), Ga internal standard was then added. Homogenization was done in ultrasonic bath, before 8 µl were deposited on a siliconized quartz carrier and dried at 100° C on a hot plate. The sample was measured in triplicate with a 300 s integration time per specimen.

Results are reported in Table 3 and Fig. 6 and 7: relative standard deviation is within 10% for certified values and recovery too for transition metals. K and Ca larger deviations may be either related to a small matrix effect, which actually affects more low fluorescence energies, or to the different speed of sedimentation for K and Ca-bearing solid phases in the slurry (e.g. carbonate).

Table 3. Results for NIST 2781 prepared as a slurry.

		Reference value	Exp. Mean	Std. Dev.	RSD(%)
K	%	0.49	0.61	0.07	12.15
Ca	%	3.9	3.31	0.06	1.86
Cr	mg/kg	202	187.00	18.54	9.90
Fe	%	2.8	2.79	0.09	3.16
Ni	mg/kg	80.2	88.00	1.16	1.07
Cu	mg/kg	627	614.80	18.41	3.00
Zn	mg/kg	1273	1215.11	21.44	1.76
Pb	mg/kg	200.8	205.78	6.70	3.25
Se	mg/kg	16	13.43	0.95	7.08

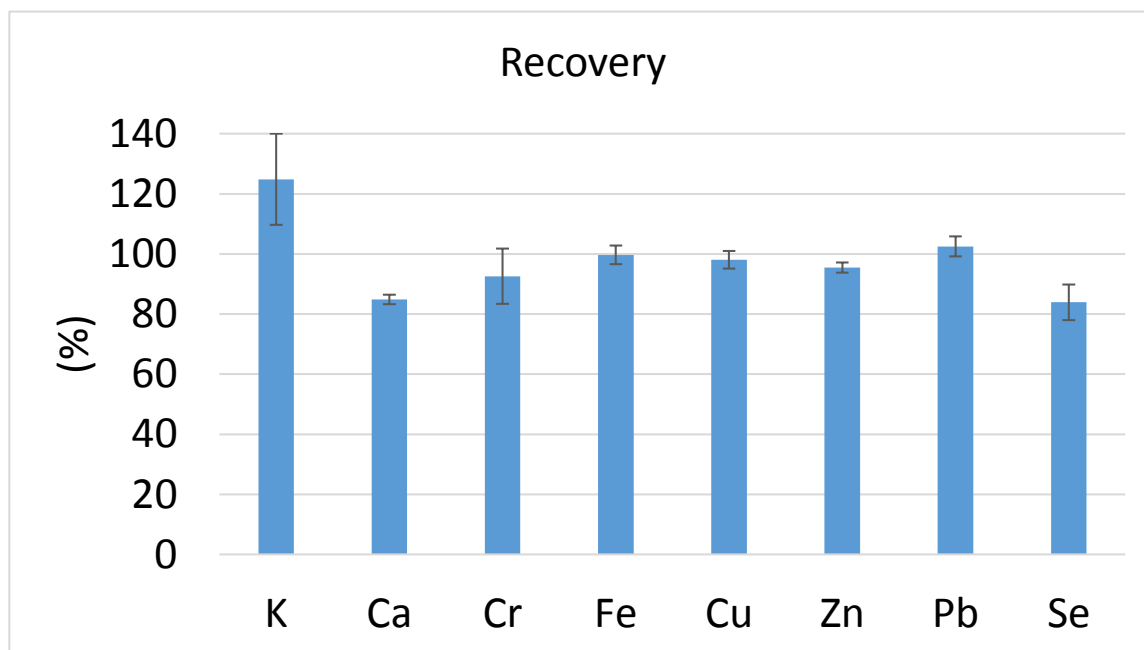


Fig.6. Recovery values for NIST 2781.

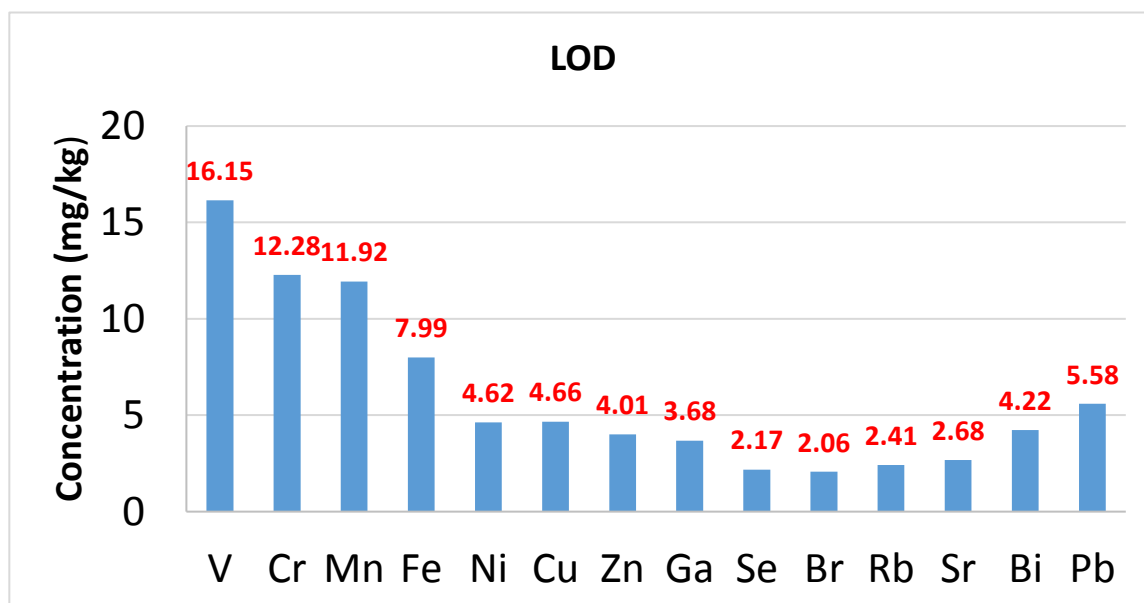


Fig.7. Detection limits for NIST 2781.

6. Comments and Conclusions

Some environmental applications of TXRF have been shown by using the Horizon spectrometer, which, coupled with a suitable sample preparation, is an effective analytical solution.

In this work, LOD was calculated according to the following formula:

$$c_{LOD,x} = \frac{3}{N_x} c_x \sqrt{N_{back}} = \frac{3}{N_{IS} S_{x,IS}} c_{IS} \sqrt{N_{back}} = c_{LOD,x} = \frac{3}{R_{IS} S_{x,IS}} c_{IS} \sqrt{\frac{R_{back}}{t}}$$

where N_{IS} and N_x are the integrated areas of the representative peak for internal standard and the analyte x , whose relative sensitivity is $S_{x,IS}$. N_{back} is the background area below the analyte peak and c_{IS} the known concentration of the internal standard. By increasing the count rate R , it is possible to keep the same LOD at reduced measurement time t : a doubled detector area should speed up the data collection by a factor 1.41.

If Na, Mg and Al are to be estimated, a multiple radiation (Mo/W) instrument is suggested, so that $W L\alpha$ in He flux can be used to both maximize the fluorescence yield from low Z elements and $L\alpha$ lines of larger ones. Cd can be determined either by $L\alpha$ or $K\alpha$ lines: the previous are less intense and prone to spectral interference (Ar, Ag, K), while the latter require a high energy excitation source (Bremsstrahlung radiation),

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