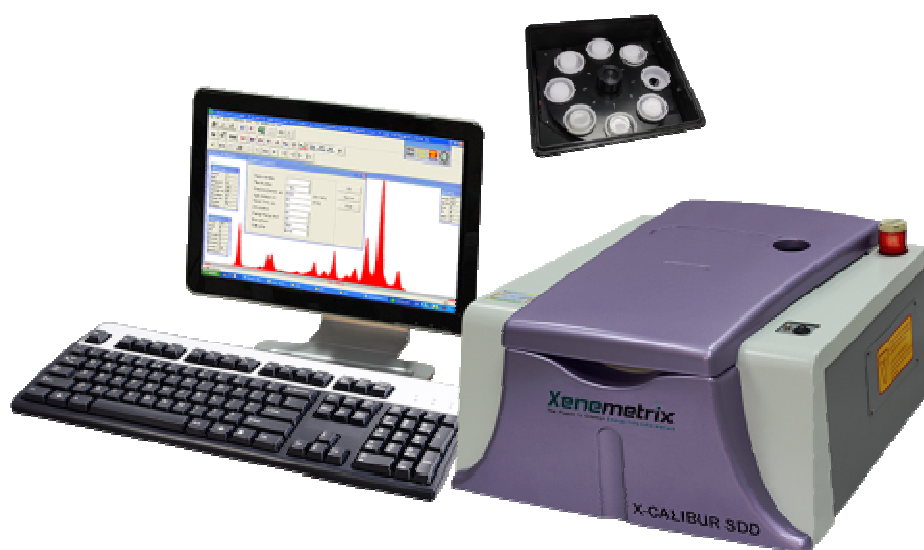


APPLICATION NOTE
XE-2012-3158

Xenometrix
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Quantitative analysis of Mo, Co, As, Pb, Hg, Cd and Cr in agricultural nutrients liquid suspensions

with X-Calibur SDD Analyzer



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ABSTRACT

Quantitative analysis of Mo, Co, As, Pb, Hg, Cr and Cd in agricultural nutrients was performed using Xenometrix EDXRF analyzer, model X-Calibur equipped with a Silicone Drift Detector.

OBJECTIVES

1. To develop a quick and robust quantitative method for analysis of Mo, Co, As, Pb, Hg, Cr and Cd in agricultural nutrients samples using EDXRF analytical technique
2. To use the calibrated X-CaliburSDD analyzer to analyze unknown samples

BACKGROUND

EDXRF is a quick non-destructive technique for qualitative elemental analysis of major and trace elements, and quantitative for most elemental contents in solids, powders or liquids.

Having the advantage of being extremely quick, easy to operate and hardly requiring any sample preparation its popularity has increased among a diverse of industries both in their quality control laboratory as well as in R&D work.

ANALYTICAL CONFIGURATION

Table 1: Analytical Configuration of X-Calibur SDD analyzer

Instrument	X-Calibur SDD EDXRF Bench top Spectrometer System
Excitation	Direct with Rh-Anode X-ray Tube, 50W/50kV.
Detector	High Performance Silicon Drift Detector (SDD) Resolution: 135eV at 5.9keV
Analysis Time	300 seconds
Environment	Air
Sample Preparation	Liquid suspension samples were prepared by customer. All samples were vigorously shaken before acquisition of spectra

EXPERIMENTALS

PREPARATIONS OF CALIBRATION STANDARDS

Three calibration standards were received from the customer. These standards were specially prepared liquid suspensions from raw materials containing all elemental components of interest in the range of concentrations of interest. From the raw material used, the concentrations of all elements of interest were calculated and to further qualify the concentrations of the three preparations, two samples of each standard were analyzed by ICP. The calculated concentrations as well as the results of the ICP analysis are shown in Tables 2a-2c. The data provided by the customer. The mean values \pm one standard deviation and relative standard deviation per two samples of each calibration standard are listed in the tables.

Table 2a: ST1 (90560104ST1) - Calculated concentrations from raw material input and measured mean concentrations by ICP.

Material added Standard ST1	Element of interest	Given (calc) Conc.	Average results by ICP	StDev ICP	%RSD ICP
Na ₂ MoO ₄ *2H ₂ O	Mo	7.26%	6.99%	0.218	3.12%
CoSO ₄ *7H ₂ O	Co	0.78%	0.69%	0.049	7.07%
3As ₂ O ₅ *5H ₂ O	As	<100 mg/kg	-	-	-
Cd(NO ₃) ₂ ICP std	Cd	<100 mg/kg	-	-	-
Pb(Ac) ₂ *3H ₂ O	Pb	<100 mg/kg	-	-	-
K ₂ CrO ₄	Cr	<100 mg/kg	-	-	-
Hg(Ac) ₂	Hg	42 mg/kg	29.1 mg/kg	2.970	10.21%

Table 2b: ST2 (90560104ST2) – Calculated concentrations from raw material and measured mean concentrations by ICP.

Material added Standard ST2	Element of interest	Given (calc) Conc.	Average results by ICP	StDev ICP	%RSD ICP
Na ₂ MoO ₄ *2H ₂ O	Mo	8.07%	7.77%	0.476	6.12%
CoSO ₄ *7H ₂ O	Co	0.99%	0.94%	0.045	4.77%
3As ₂ O ₅ *5H ₂ O	As	317 mg/kg	210 mg/kg	29.698	14.14%
Cd(NO ₃) ₂ ICP std	Cd	16 mg/kg	14.0 mg/kg	2.828	20.20%
Pb(Ac) ₂ *3H ₂ O	Pb	53 mg/kg	<0.5 mg/kg	-	-
K ₂ CrO ₄	Cr	52 mg/kg	55.3 mg/kg	7.495	13.55%
Hg(Ac) ₂	Hg	60 mg/kg	42.9 mg/kg	1.273	2.97%

Table 2c: ST3 (90560104ST3) – Calculated concentrations from raw material and measured mean concentrations by ICP.

Material added Standard ST3	Element of interest	Given (calc) Conc.	Average results by ICP	StDev ICP	%RSD ICP
Na ₂ MoO ₄ *2H ₂ O	Mo	8.46 %	8.07%	0.342	4.23%
CoSO ₄ *7H ₂ O	Co	1.08%	1.04%	0.040	3.87%
3As ₂ O ₅ *5H ₂ O	As	638 mg/kg	473 mg/kg	70.711	14.95%
Cd(NO ₃) ₂ ICP std	Cd	31 mg/kg	26.8 mg/kg	5.303	19.83%
Pb(Ac) ₂ *3H ₂ O	Pb	107 mg/kg	<0.5 mg/kg	-	-
K ₂ CrO ₄	Cr	107 mg/kg	103 mg/kg	14.142	13.73%
Hg(Ac) ₂	Hg	77 mg/kg	54 mg/kg	2.687	4.99%

CALIBRATION OF X-CALIBUR SDD

To calibrate the X-Calibur the spectra of the three calibration standards were acquired on two separate samples per standard. The standard bottle was vigorously shaken 30-60 seconds before pouring about 5-6 ml of sample into a special XRF cup with a prolene thin film support. For optimal detection of all elements three sets of acquisition parameters were used; Rh tube filter was used for optimal acquisition of Mo, As and Hg; W tube filter was found optimal for Co, Pb and Cd while the Ti filter was best for Cr. Each acquisition per each group of elements was performed 5 minutes. For calibration purpose each standard sample was acquired during 3x5min (in total 15 min). From spectral data the intensity of each elemental peak of interest was extracted and net intensity versus given concentration was plotted. Using regression analysis the best fitted calibration curve was found for each element of interest. All intensity extractions and calculations involved were done automatically by the user-friendly built-in automatic nEXt™ software. The correlation curves for each element are shown in Figures 1a-1g and the calibration data is detailed in Table 3a-3g.

Figure 1a: Mo correlation curve

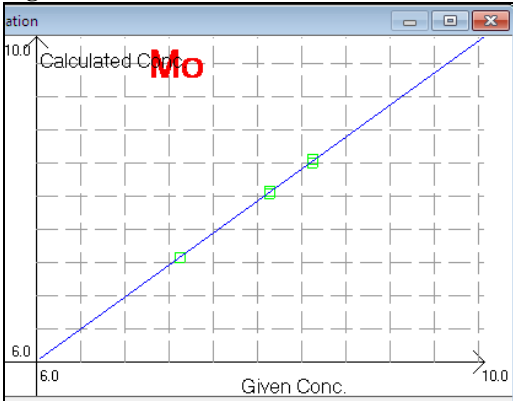


Figure 1b: Co correlation curve

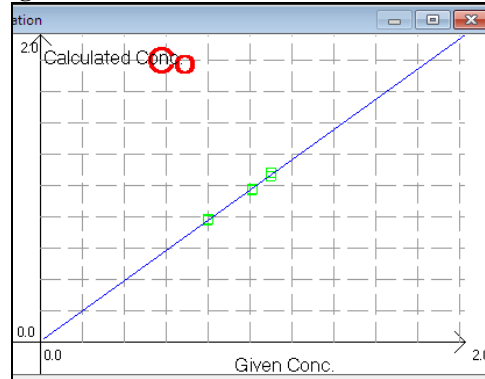


Figure 1c: Pb correlation curve

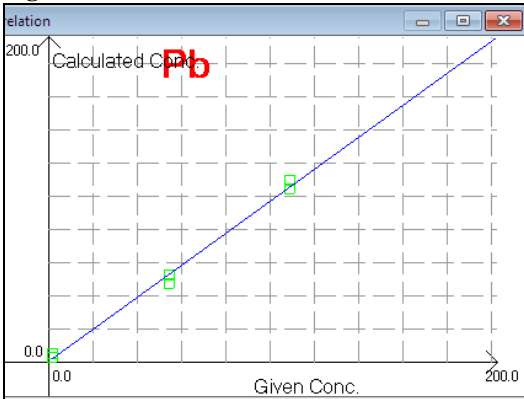


Figure 1d: Cd correlation curve

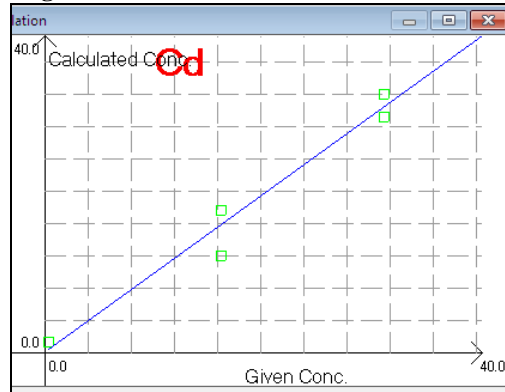


Figure 1e: As correlation curve

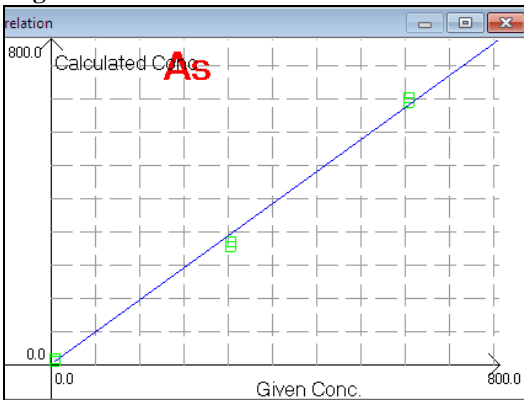


Figure 1f: Hg correlation curve

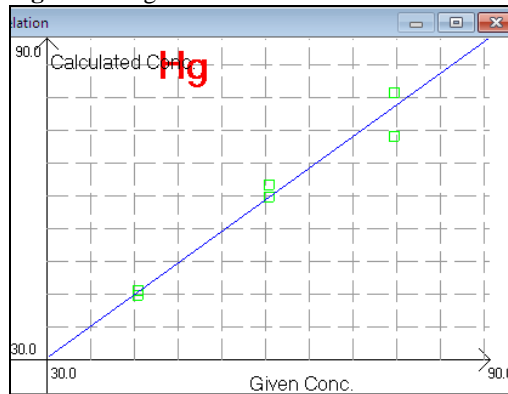


Figure 1g: Cr correlation curve

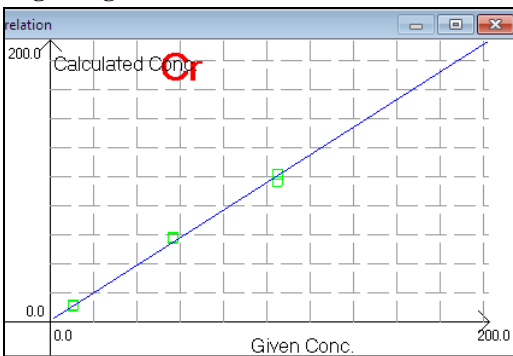


Table 3a: Calibration data of Mo, Co, Pb and Cd in pesticide standards

	Mo wt% correlation 0.9994 std.dev.= 0.017, rsd=0.22%			Co wt% correlation 0.9977 std.dev.= 0.0085, rsd=0.94%			Pb mg/kg correlation 0.9971 std.dev.= 3.3, rsd=5.4%			Cd mg/kg correlation 0.9866 std.dev.= 2.07 rsd=12.6%		
	Given	Calc'd	mean±sd rsd%	Given	Calc'd	mean±sd rsd%	Given	Calc'd	mean±sd rsd%	Given	Calc'd	mean±sd rsd%
ST1a	7.26	7.26	7.26±0.01 0.08%	0.78	0.78	0.78±0.01 0.71%	0.0	3.1	Not relevant	0.0	1.01	1.02±0.01 1.2%
ST1b	7.26	7.26		0.78	0.79		0.0	0.94		0.0	1.03	
ST2a	8.07	8.09	8.07±0.03 0.34%	0.99	0.98	0.98±0.01 0.61%	53.0	47.1	49.6±3.5 7.0	16	17.8	14.9±4.1 27.3%
ST2b	8.07	8.05		0.99	0.99		53.0	52.0		16	12.1	
ST3a	8.46	8.48	8.46±0.03 0.36%	1.08	1.09	1.08±0.01 1.34%	107.0	111.2	108.4±4.0 3.7%	31	32.6	31.1±2.1 6.9%
ST3b	8.46	8.44		1.08	1.07		107.0	105.5		31	29.6	

Table 3b: Calibration data of As, Hg, Cr in pesticide standards

	As mg/kg correlation 0.9981 std.dev.= 16.8 rsd=5.2%			Hg mg/kg correlation 0.9820 std.dev.= 2.7 rsd=4.0%			Cr mg/kg correlation 0.9971 std.dev.= 2.6 rsd=5.3%		
	Given	Calc'd	mean±sd rsd%	Given	Calc'd	mean±sd rsd%	Given	Calc'd	mean±sd rsd%
ST1a	0.0	0.0	<10 mg/kg	42.0	41.6	42.0±0.5 1.3%	9.0	8.9	9.3±0.5 5.9%
ST1b	0.0	8.5		42.0	42.4		9.0	9.7	
ST2a	317.0	297.9	292.3±8.01 2.7%	60.0	62.4	61.3±1.5 2.5%	55.0	58.7	58.1±0.9 1.5%
ST2b	317.0	286.6		60.0	60.2		55.0	57.5	
ST3a	638.0	641.8	649.0±10.1 1.6%	77.0	79.8	75.7±5.8 7.7%	103.0	103.9	101.1±3.9 3.8%
ST3b	638.0	656.1		77.0	71.6		103.0	98.4	

RESULTS AND DISCUSSION

The calibrated X-Calibur SDD was used to analyze the unknown sample preparation SA (90560104SA). Two samples of SA were analyzed separately on X-Calibur and the individual results together with mean value, standard deviation and relative standard deviation in % are shown in Table 4. The elements As, Cd and Pb were hardly detected on sample SA.

QUANTITATIVE ANALYSIS OF UNKNOWN SAMPLE

Table 4: Analysis of sample SA(90560104SA) on X-Calibur SDD

	SA_a	SA_b	mean±std	RSD%
Mo	7.95	7.91	7.93±0.02	0.31%
Co	0.86	0.85	0.85±0.01	1.2%
As	0.0	3.4	< 10 mg/kg	-
Cd	1.1	1.1	< 10 mg/kg	-
Pb	3.0	0.0	< 10 mg/kg	-
Cr	11.9	10.6	11.2±0.90	8.03
Hg	41.6	41.6	41.6±0.0	NA

PRECISION

In order to evaluate the repeatability of the analyzer and the reproducibility of samples the following investigations were performed.

Repeatability experiment

One and the same sample, i.e. 6ml of ST2 in an XRF sample cup was measured and analyzed nine times consecutively without moving the sample in between the measurements. The individual result of each measurement and the mean value \pm standard deviation, relative standard deviation and the relative accuracy are presented in Table 5.

As shown in the Table, the liquid suspension was not enough stable in order to investigate the repeatability (precision) of the analyzer. The measured value increased during the 45 minutes of experiment, most probably due to “precipitation” of material at the bottom of the cup (closest to the x-ray beam). However the mean value and the precision obtained was still reasonable.

Reproducibility

To evaluate the reproducibility of different samples, four different samples from ST2 bottle was poured into XRF sample cups and measured once per cup. The individual results, the mean value \pm standard deviation, relative standard deviation and relative accuracy are listed in Table 6.

Table 5: Repeatability experiment. Nine consecutive measurements of standard ST2 without moving the sample in between

	Mo wt%	Co wt%	As mg/kg	Pb mg/kg	Hg mg/kg	Cd mg/kg	Cr mg/kg
mean \pm sd	8.41 \pm 0.16	1.05 \pm 0.05	321.1 \pm 24.8	58.6 \pm 3.8	54.6 \pm 7.2	15.1 \pm 3.4	59.4 \pm 3.2
rsd%	1.9%	4.6%	7.7%	6.4%	13.2%	22.4%	5.3%
Given conc	8.07 %	0.99 %	317 mg/kg	53 mg/kg	60 mg/kg	16 mg/kg	52 mg/kg
Rel. accuracy	4.2%	6.0%	1.3%	10.6%	9.0%	5.6%	14.2%
Elapsed time							
5 min	8.18	0.97	283.1	54.0	48.1	15.0	57.5
10 min	8.27	0.98	308.8	61.8	61.6	18.3	55.9
15 min	8.29	1.02	286.2	54.9	60.5	17.3	59.3
20 min	8.37	1.04	334.7	59.1	52.2	10.5	57.0
25 min	8.41	1.06	351.2	56.4	66.3	16.8	60.3
30 min	8.43	1.07	311.8	56.6	49.3	9.3	57.5
35 min	8.51	1.08	337.6	63.0	57.9	17.4	59.7
40 min	8.61	1.08	333.2	56.7	45.2	13.1	61.0
45 min	8.65	1.11	343.7	64.6	50.2	18.0	66.6

Table 6: Reproducibility. Four different samples of standard ST2 were measured

Four samples	Mo wt%	Co wt%	As mg/kg	Pb mg/kg	Hg mg/kg	Cd mg/kg	Cr mg/kg
mean \pm sd	8.10 \pm 0.06	0.98 \pm 0.01	290.0 \pm 6.6	52.8 \pm 4.5	69.1 \pm 25	14.7 \pm 2.4	58.0 \pm 0.6
rsd%	0.71%	0.81%	2.3%	8.6%	36.4%	16.6%	1.0%
Given conc	8.07 %	0.99 %	317 mg/kg	53 mg/kg	60 mg/kg	16 mg/kg	52 mg/kg
Rel. accuracy	0.4 %	1.0 %	8.5 %	0.4%	15.2%	8.1%	11.5%
ST2_a	8.09	0.98	297.9	47.1	62.4	17.8	58.7
ST2_b	8.05	0.99	286.6	52.0	60.2	12.1	57.5
ST2_c	8.08	0.97	292.6	54.0	105.5	15.0	58.2
ST2_d	8.18	0.98	283.1	58.0	48.1	13.7	57.5

SPECTRA

A few typical spectra are shown below in Figure 1-3

Figure 1: Sample ST3 acquired with Rh x-ray tube filter

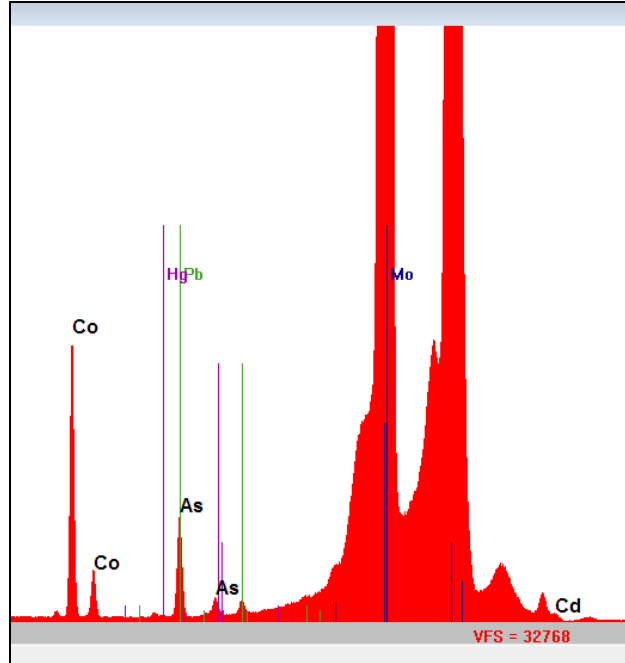


Figure 2: Sample ST3 acquired with Ti x-ray tube filter

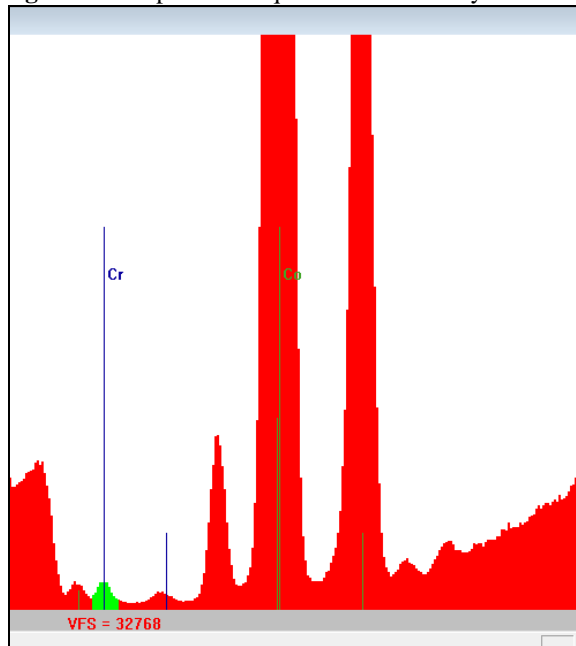
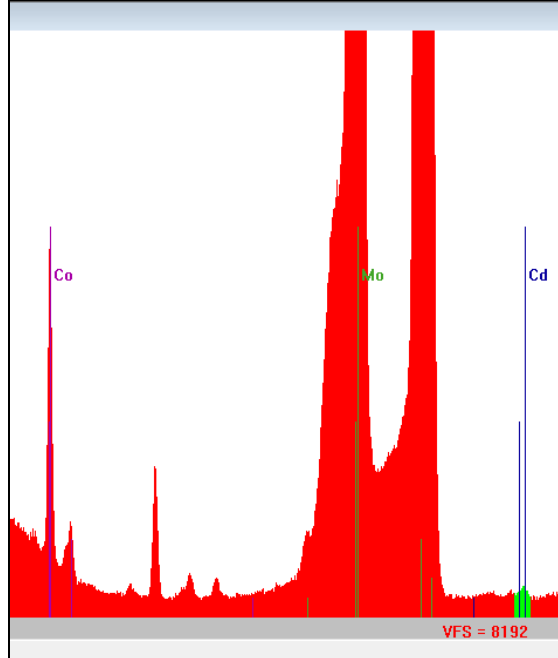


Figure 3: Sample ST3 acquired with W x-ray tube filter



CONCLUSIONS

A few conclusions can be made from this study:

- 1) Very good accurate and repeatable results are received using EDXRF analysis on liquid pesticide suspensions
- 2) Material in the suspensions is precipitating with time and therefore not more than 10-15 minutes max should be spent on each sample in the spectrometer.
- 3) Comparing results with the ICP results obtained from the customer show that EDXRF results are more accurate and show better precision than the ICP results.
- 4) Very low concentrations (<100mg/kg) that sometimes are not detected by ICP are “easily” detected in the EDXRF spectrum and corresponding concentrations are measured. (compare results on ST1).

In summary Xenometrix EDXRF analyzer X-Calibur is an excellent tool for fast, accurate and reliable measurements on liquid pesticide suspension samples.