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Air pollution

STATIONARY SOURCES EMISSIONS. TOTAL Cd, Cr, Cu DETERMINATION IN EXHAUST GASES FROM INCINERATORS

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Abstract. Dust sample containing Cd, Cr and Cu is isokinetically withdrawn from an evacuation chimney/duct. The sampling step is followed by laboratory analyses for metal determination. Before the sampling and analyses steps, the main aspects of chromium, cadmium and copper determination in residual effluents were established.

Keywords: heavy metals, emissions, incineration.

EXPERIMENTAL

Isokinetic sampling[1,2]. First step for a pollutant determination is to extract (to sample) the pollutant from the gaseous residual effluent or from the ambient air. The sampling device is wormed up to operation temperature. The initial gas volume is recorded and then sampling is started. Nozzle should be in the gas stream, against flow stream. During sampling, at each 5 min the temperature and gas flow are checked and, if necessary, sampling flow is regulated as necessary to maintain isokinetic sapling rate. When manipulate the sample special attention should be paid to dust losses and sample contamination.

After sampling, the sampling device is turned off and pulled off from the stack. The filter should be removed at the first nearest site without sample contamination risk.

All the parts which are in contact with the sampled gas are washed with acid. The washing acid is collected in an identifiable bottle. After the washing with acid, the nozzle, the sample probe and filter householder are cleaned up with water and acetone and then dried.

The absorbing solutions are collected together in an identifiable bottle except the solution from the last impinger which is collected separately to check up the absorption efficiency.

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Samples preparation for analyses[3]. For correct determination of the metals contents in the residual gas the absorbing and washing solutions should be analysed separately and the final result is a sum of these results.

The retained metals on the filter, in soluble or insoluble particulate matters, form re-extracted or digested with different acids mixture:

– nitric acid extraction;

– total digestion with nitric acid: hydrofluoric acid mixture;

– extraction in nitric acid: hydrochloric acid mixture, on temperature controlled heating plate or using microwave digestion and then are quantitatively transferred in 50-ml glass or PTFE marked flasks for analyses.

When hydrofluoric acid digestion is used for fill up the flasks hydroboric acid is used.

The absorbing solutions are transferred in borosilicate bikers and digested for 1 h on heating plate covered with watch glass, then are quantitatively transferred in 50-ml glass or PTFE marked flasks for analyses. Washing solutions are similarly treated, but are kept on the heating plate until the right volume for analyses is reached.

At the same time, a blank is prepared using an unexposed filter from the same lot as those used for sampling.

Experiments for determination of Cd, Cr and Cu from waste incineration by FAAS. The methods for determination of Cd, Cr and Cu from acid solutions obtained as described before include the following steps:

– drawing up of calibration curves using the specific conditions for each metal and performance characteristics determination;

– limit of quantification and detection determination;

– fidelity determination (repeatability and reproducibility);

– recuperation yield determination.

Copper determination by FAAS[4–11]. For drawing up the calibration curve 5 standards of 1, 2, 3, 4 and 5 mg Cu/l were prepared using the same acid matrix as that of the samples. The standards were analysed by FAAS and the obtained values for each standard were used to draw the calibration curve (Fig. 1). The results are presented in Table 1.

Table 1. Results for Cu calibration curve (λ = 324.7 nm)

No	Obtained extinctions for different mg Cu content / l solution:				
	1	2	3	4	5
1	0.09312	0.19920	0.30232	0.40291	0.48910
2	0.09287	0.19927	0.30228	0.40289	0.48904
3	0.09298	0.19917	0.30223	0.40296	0.48917
4	0.09322	0.19921	0.30239	0.40284	0.48909
5	0.09316	0.19919	0.30232	0.40290	0.48911
Mean value	0.09307	0.19921	0.30230	0.40290	0.48910

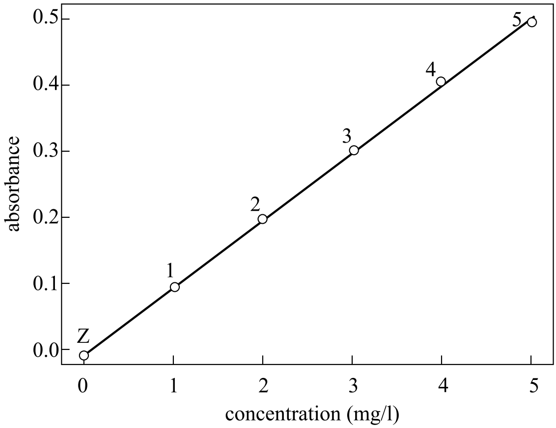

Fig. 1. Calibration curve for Cu

Using the data from Table 1 the following performance characteristics were calculated:

- calculated reagents witness: $a = 0.001411$
- method sensitivity: $b = 0.098635$
- residual standard deviation: $S_y = 0.278381$
- standard methods deviation: $S_{x0} = 2.822338$

All the performance characteristics are presented in Table 2

Detection and quantification limit of metal determination. For evaluating the detection and quantification limit, the absorbance for 10 parallel standards were determined. Using the obtained results the standard deviation and the limits were calculated according to Table 3, considering LOD $=x_m+3s$ and LOQ $= x_m+10s$.

Methods sensitivity determination. The method sensitivity represents the calibration curve slope and it is represented by the calibration curve *b* coefficient value. For this method b=0.098635 AU/µg Cu, which means that 0.01 AU correspond to 0.10 mg Cu.

Fidelity and recovery determination. To estimate the methods fidelity, the results obtained in the Proficiency Test CALITAX–LABAQUA – Round II – June 2005 were used. For repeatability determination 3 results obtained by the Air Pollution laboratory in the above mentioned PT were used. The repeatability was expressed as standard deviation (r_s) and as relative repeatability (r_{rel}, %). For relative recovery determination the true value communicated by the PT organiser, 19.55 µg/ filter, was used. The results are presented in Table 4.

Table 2. Methods performance characteristics

Data: 20/11/2005
Calibration curve: Cu
Apparatus: FLAAS

xi	yi	xi-X	(xi-X)2	yi-Y	(xi-X)(yi-Y)	(yi-Y)2	bxi	y^I	yi-y^I	(yi-y^I)2
1	0.09307	–2	4	–0.204250	0.408492	0.041716	0.098635	0.100046	–0.006980	4.87E-05
2	0.19921	–1	1	–0.098110	0.098106	0.009625	0.19727	0.198681	0.000529	2.8E-07
3	0.30230	0	0	0.004984	0	2.48E-05	0.295905	0.297316	0.004984	2.48E-05
4	0.40290	1	1	0.105584	0.105584	0.011148	0.39454	0.395951	0.006949	4.83E-05
5	0.48910	5	25	0.489100	2.4455	0.239219	0.007056	0.007056	0.482044	0.232366
Medium X	Medium Y		Sum		Sum					Sum
3	0.297316		31		3.057682					0.232488
b =	0.098635		bX	0.295905						
a =	0.001411									
Sy (mg/l)	0.278381		Sx0	2.822338						

Table 3. LOD and LOQ

	Blank	LOD+LOQ			
xm	xm-X	(xm-X)2		x=	0.008624
0.00862	–4E-06	1.6E-11		s=	0.000134
0.00844	–2E-04	3.39E-08		2s=	0.000268
0.00887	0.0002	6.05E-08		3s=	0.000402
0.00853	–9E-05	8.84E-09		4s=	0.000535
0.00867	5E-05	2.12E-09		5s=	0.000669
0.00858	–4E-05	1.94E-09		6s=	0.000803
0.00877	0.0001	2.13E-08		10s=	0.001338
0.00872	1E-04	9.22E-09	LOD	x+3s=	0.009026
0.00855	–7E-05	5.48E-09		x+4s=	0.009159
0.00849	–1E-04	1.8E-08		x+5s=	0.009293
Mean xm		1.61E-07		x+6s=	0.009427
0.008624			LOQ	x+10s=	0.009962

Table 4. Calculated values for standard deviation of repeatability, recovery

No	Cu (mg/l)
1	18.5
2	18.65
3	18.55
Mean	18.56667
r(s)	0.076376
r_{rel} (%)	0.411362
Recovery (%)	94.93

For reproducibility calculations were used 7 results obtained by 7 different laboratories using the same method, FAAS (Table 5).

Table 5. Calculated values for reproducibility standard deviation and relative reproducibility

No	Cu (mg/l)
1	19.33
2	18.57
3	19.53
4	20.82
5	18.5
6	21
7	19.24
Mean	19.57
Reprod.	0.993345
Rel. reprod. (%)	5.075853

Chromium determination by FAAS[12–15]. For drawing up the calibration curve 5 standards of 1, 2, 3, 4 and 5 mg Cr/l were prepared using the same acid matrix as that of the samples. The standards were analysed by FAAS and the obtained values for each standard were used to draw the calibration curve (Fig. 2). The results are presented in Table 6.

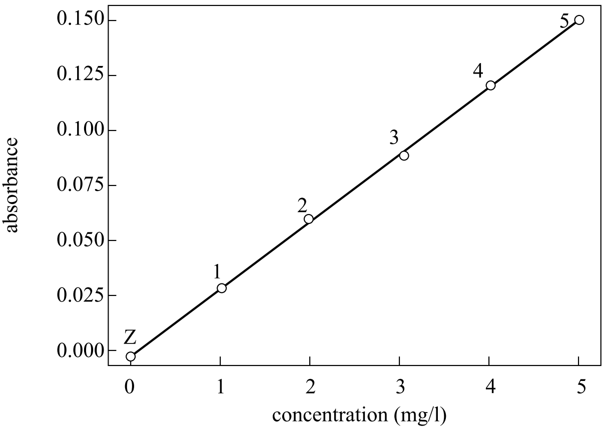

Fig. 2. Calibration curve for Cr

Table 6. Results for Cr calibration curve (λ = 357.9 nm)

No	Obtained extinctions for different mg Cr content / l solution:				
	1	2	3	4	5
1	0.02556	0.05729	0.08392	0.11456	0.14570
2	0.02562	0.05737	0.08382	0.11464	0.14631
3	0.02547	0.05745	0.08374	0.11448	0.14687
4	0.02573	0.05723	0.08397	0.11469	0.14521
5	0.02562	0.05735	0.08390	0.11464	0.14611
Mean value	0.02560	0.05734	0.08387	0.11460	0.14604

Using the data of Table 6 the following methods performance characteristics were calculated:

– calculated reagents witness: $a = -0.00231$
– method sensitivity: $b = 0.029266$
– residual standard deviation: $S_y = 0.090988$
– standard methods deviation: $S_{x0} = 3.10901$

All the performance characteristics are presented in Table 7.

Detection and quantification limit of Cr determination. The detection and quantification limits of Cr determination were evaluated on the basis of the absorbance for 10 parallel standards. Using the obtained results the standard deviation and the limits were calculated according to Table 8, considering LOD $=x_m+3s$ and LOQ $= x_m+10s$.

Table 7. Methods performance characteristics

Data: 20/11/2005
Calibration curve Cr
Apparatus: FLAAS

xi	yi	xi-X	(xi-X)2	yi-Y	(xi-X)(yi-Y)	(yi-Y)2	bxi	y^I	yi-y^I	(yi-y^I)2
1	0.0256	–2	4	–0.05989	0.11978	0.003587	0.029266	0.026958	–0.00136	1.85E-06
2	0.05734	–1	1	–0.02815	0.02815	0.000792	0.058532	0.056224	0.001116	1.25E-06
3	0.08387	0	0	–0.00162	0	2.62E-06	0.087797	0.08549	–0.00162	2.62E-06
4	0.1146	1	1	0.02911	0.02911	0.000847	0.117063	0.114756	–0.00016	2.43E-08
5	0.14604	5	25	0.14604	0.7302	0.021328	–0.01154	–0.01154	0.157577	0.024831
Medium X	Medium Y		Sum		Sum					Sum
3	0.08549		31		0.90724					0.024836
b=	0.029266		bX	0.087797						
a=	–0.00231									
Sy (mg/l)	0.090988		Sx0	3.10901						

Table 8. LOD and LOQ

	Blank	LOD+LOQ			
xm	xm-X	(xm-X)2		x=	0.006752
0.00682	6.8E-05	4.6E-09		s=	0.000218
0.00642	–0.0003	1.1E-07		2s=	0.000436
0.0072	0.00045	2E-07		3s=	0.000654
0.00695	0.0002	3.9E-08		4s=	0.000873
0.00657	–0.0002	3.3E-08		5s=	0.001091
0.00672	–3E-05	1E-09		6s=	0.001309
0.00667	–8E-05	6.8E-09		10s=	0.002181
0.00658	–0.0002	2.9E-08	LOD	x+3s=	0.007407
0.00679	3.8E-05	1.4E-09		x+4s=	0.007625
0.0068	4.8E-05	2.3E-09		x+5s=	0.007843
Mean xm		4.3E-07		x+6s=	0.008061
0.00675			LOQ	x+10s=	0.008934

Methods sensitivity determination. The method sensibility represents the calibration curve slope and it is represented by the calibration curve *b* coefficient value. For this method b=0.029266 AU/µg Cr, which means that 0.01 AU correspond to 0.34 mg Cr.

Fidelity and recovery determination. To estimate the methods fidelity, the results obtained in the Proficiency Test CALITAX – LABAQUA – Round II – June 2005 were used. For repeatability determination 3 results obtained by the Air Pollution laboratory in the above mentioned PT were used.

The repeatability was expressed as standard deviation (r_s) and as relative repeatability (r_{rel}, %) . For relative recovery determination the true value communicated by the PT organiser, 345 µg/ filter, was used. The results are presented in Table 9.

Table 9. Calculated values for standard deviation of repeatability, recovery

No	Cr (mg/l)
1	365
2	360
3	358
Mean	361
r(s)	3.605551
r_{rel} (%)	0.998768
Recovery (%)	104

For reproducibility calculation were used 7 results obtained by 7 different laboratories using the same method, FAAS. In Table 10 are presented the calculations and the obtained results.

Table 10. Calculated values for reproducibility standard deviation and relative reproducibility

No	Cr (mg/l)
1	487
2	361
3	428
4	400
5	420
6	410
7	422
Mean	418.2857
Reprod.	37.6772
Rel. reprod. (%)	9.01

Cadmium determination by FAAS[16–20]. For drawing up the calibration curve 5 standards of 0.1, 0.2, 0.3, 0.4 and 0.5 mg Cd/l were prepared using the same acid matrix as that of the samples. The standards were analysed by FAAS and the obtained values for each standard were used to draw the calibration curve (Fig. 3). The results are presented in Table 11.

Table 11. Results for Cd calibration curve ($\lambda = 228.8$ nm)

No	Obtained extinction for different mg Cd content / l solution:				
	0.1	0.2	0.3	0.4	0.5
1	0.02394	0.04910	0.07718	0.10173	0.12663
2	0.02401	0.04926	0.07707	0.10146	0.12690
3	0.02387	0.04921	0.07711	0.10145	0.12677
4	0.02408	0.04906	0.07716	0.10122	0.12676
5	0.02397	0.04931	0.07722	0.10154	0.12654
Mean value	0.02397	0.04919	0.07715	0.10148	0.12672

Using the data of Table 11 the following methods performance characteristics were calculated:

- calculated reagents witness: $a = -0.00068$
- the method sensitivity: $b = 0.254599$
- residual standard deviation: $S_y = 0.073354$
- standard methods deviation: $S_{x0} = 0.288117$

All the performance characteristics are presented in Table 12.

Table 12. Methods performance characteristics

Data: 20/11/2005

Calibration curve Cd

Apparatus FLAAS

xi	yi	xi-X	(xi-X)2	yi-Y	(xi-X)(yi-Y)	(yi-Y)2	bxi	y^I	yi-y^I	(yi-y^I)2
0.1	0.02398	–0.2	0.04	–0.05172	0.010345	0.002675	0.02546	0.024784	–0.0008	6.47E-07
0.2	0.04919	–0.1	0.01	–0.02651	0.002651	0.000703	0.05092	0.050244	–0.00105	1.11E-06
0.3	0.07715	0	0	0.001446	0	2.09E-06	0.07638	0.075704	0.001446	2.09E-06
0.4	0.1015	0.1	0.01	0.025796	0.00258	0.000665	0.10184	0.101164	0.000336	1.13E-07
0.5	0.1267	0.5	0.25	0.1267	0.06335	0.016053	0.00034	–0.00034	0.127038	0.016139
Medium X	Medium Y		Sum		Sum					Sum
0.3	0.075704		0.31		0.078926					0.016143
b=	0.254599		bX	0.07638						
a=	–0.00068									
Sy (mg/l)	0.073354		Sx0	0.288117						

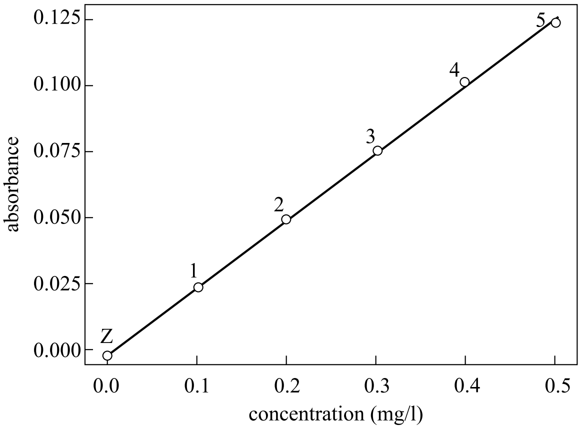

Fig. 3. Calibration curve for Cd

Detection and quantification limit determination. The detection and quantification limits are determined using the absorbance valued of 10 parallel standards. On the basis of the obtained results, the standard deviation and limits were calculated according to Table 13, considering LOD =x_m+3s and LOQ = x_m+10s.

Table 13. LOD and LOQ

	Blank	LOD+LOQ			
xm	xm-X	(xm-X)2		x=	0.002238
0.00239	0.00015	2.3104E-08		s=	0.000228
0.00186	–0.0004	1.4288E-07		2s=	0.000457
0.00251	0.00027	7.3984E-08		3s=	0.000685
0.00213	–0.0001	1.1664E-08		4s=	0.000914
0.00194	–0.0003	8.8804E-08		5s=	0.001142
0.00246	0.00022	4.9284E-08		6s=	0.001371
0.00225	1.2E-05	1.44E-10		10s=	0.002285
0.00207	–0.0002	2.8224E-08	LOD	x+3s=	0.002923
0.00232	8.2E-05	6.724E-09		x+4s=	0.003152
0.00245	0.00021	4.4944E-08		x+5s=	0.003380
Mean xm		4.6976E-07		x+6s=	0.003609
0.00224			LOQ	x+10s=	0.004523

Methods sensitivity determination. The method sensitivity represents the calibration curve slope and it is represented by the calibration curve *b* coefficient value. For this method *b*=0.254599 AU/µg Cr, which means that 0.01 AU correspond to 0.039 mg Cd.

Fidelity and recovery determination. To estimate the methods fidelity the results obtained in the Proficiency Test CALITAX – LABAQUA – Round I – April. 2005 were used. For repeatability determination 3 results obtained by the Air Pollution laboratory in the above mentioned PT were used

The repeatability was expressed as standard deviation (r_s) and as relative repeatability (r_{rel}, %) . For relative recovery determination the true value communicated by the PT organiser, 8.32 μg/ filter, was used. The results are presented in Table 14.

Table 14. Calculated values for standard deviation of repeatability, recovery

No	Cd (mg/l)
1	9.25
2	9.3
3	9.2
Mean	9.25
r(s)	0.05
r_{rel} (%)	0.540541
Recovery (%)	111.1779

For reproducibility calculation were used 7 results obtained by 7 different laboratories using the same method, FAAS. In Table 15 are presented the calculated and obtained results.

Table 15. Calculated values for reproducibility standard deviation and relative reproducibility

No	Cd (mg/l)
1	7.77
2	9.25
3	7.53
4	8.01
5	7.33
6	8.87
7	7.63
Mean	8.055714
Reprod.	0.725416
Rel. reprod. (%)	9.004988

CONCLUSIONS

Concerning determination of metals from stationary emission sources in 2004 in Romania was adopted by confirmation sheet method the European standard EN 14385 concerning the determination of total metal concentrations from stationary emission sources.

The goal of the present project was to test this method to determine some heavy metals from incinerators emissions. For a correct quantification of the emissions value of the metals from incinerators which are in very low limits according to the Governmental Decision No 128/2002 it is necessary to use sensitive and selective analytical techniques, in this category being included FAAS and GFAAS.

The application of FAAS for metal determination from residual gases ensures:

- low detection limits comparing with other methods;
- determination of more metals from a small sample which is characteristic for dust emission sampling.

The project scope was to assure the necessary environment to apply adequate methods, sensitive and accurate, for pollutants determination based on laboratory experiments, on site sampling and statistical calculations.

From technical point of view isokinetic sampling for particulate matter collection and FAAS for quantitative analytical determination were used. For isokinetic sampling a complex sampling train has been used. This sampling train permits trapping of dust-containing metals on filters and retention of volatile metals species in a solution of hydrogen peroxide and potassium permanganate. Isokinetic sampling was performed according to the with EN 13284-1:2001 standard.

There were performed laboratory experiments for methods characteristic determination used in Cd, Cr and Cu determination, respectively:

– limit of quantification and detection determination;
– fidelity determination (repeatability and reproducibility);
– recuperation yield determination.

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