



The Determination of Cd, Cr, Cu, Ni and Pb in a Concentrated $\text{CaCl}_2/\text{NaCl}$ Solution by AAS

Application Note

Atomic Absorption

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Summary

In the manufacture of soda by the ammonia-soda process, a solution containing suspended material is obtained. The main constituents of this caustic suspension are calcium chloride and sodium chloride in the solution, and CaCO_3 and Ca(OH)_2 in the suspended material. According to Federal discharge regulations¹, the following heavy metals must be determined in this almost saturated solution: Cd, Cr, Cu, Ni and Pb.

The measurement of these elements in such a high solids containing solution presents problems. In flame AAS, problems of rapid burner blockage are encountered. The nebulizer will also be adversely affected by the high chloride content of the matrix. Furthermore, the above listed elements must all be determined close to their detection limits.

Three methods for the solution to this analytical problem are available:

- Indirect flame atomisation
- Direct flame atomisation
- Graphite furnace atomisation



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Instrumentation and Chemicals

All measurements were carried out with an Agilent SpectrAA20B Atomic Absorption Spectrometer. The instrument parameters are presented in Table 1. A GTA-96 graphite furnace atomizer was used for some measurements.

Table 1. Instrument Parameters for Elements

Element	Wavelength (nm)	Slit width (nm)	Lamp current (mA)
Cd	228.8	0.5	3
Cr	357.9	0.2	3
Cu	324.8	0.5	2
Ni	232.0	0.2	4
Pb	217.0	1.0	5

Deuterium background correction was used in the determination of all the elements. Chemicals of purity grades "p.a." and "Suprapur" were used.

Pre-concentration and Flame Measurements Extraction of Cd, Cu, Ni and Pb

250 mL of the sample was filtered through a Macherey and Nagel "Blackband" filter. The filtrate was set aside. The residue was treated by back-flushing with HNO₃ (65%) and evaporated to dryness. The residue was then taken up in 15 mL HCl (37%) and 10 mL HNO₃ (65%) and once more evaporated to dryness. After dissolution of the sample residue in 100 mL of 7M HCl, the Fe was extracted with 50 mL methyl iso-butyl ketone (MIBK). The aqueous phase was evaporated down to about 50 mL and filtered through a "Whiteband" filter into the original filtrate.

After the addition of 25 mL of CH₃COONH₄ solution (20%), the sample was adjusted to a pH of 4 to 6 with NH₃ and CH₃COOH.

The sample was finally extracted in a separation funnel with 10 mL diethylammonium-N,N-diethyldithiocarbamate solution (1% aqueous solution) and 50 mL MIBK. Both extracts were combined and made up to 100 mL.

The ketone phases were measured by flame AAS. It should be noted that the nebulizer adjustment should be set in the high solids mode. That is, with the thimble turned clockwise as far as possible. The gap between the glass bead and the nebulizer venturi should be between 3 and 5 mm. The liquid trap was filled with MIBK which also served as the rinse solution.

To clean the nebulizer, water must be aspirated for approximately 2 seconds after each measurement. A reagent blank must also be prepared and measured. The samples were measured against a calibration graph which was obtained with measurements on matrix-compensated standards. Table 2 shows the calibration data for Cd.

Table 2. Calibration Data for Cd

Sample	Conc ppm Cd	%RSD	Mean Abs	Readings	
Blank	0.0000		-0.001	-0.002	-0.002
Standard 1	0.0200	0.4	0.034	0.034	0.034
Standard 2	0.0400	3.5	0.060	0.062	0.060
Standard 3	0.0800	0.4	0.127	0.127	0.126
Standard 4	0.2000	0.0	0.307	0.308	0.309

Co-precipitation, Pre-concentration of Cr

200 mL of the caustic solution were acidified with 20 mL HCl (37%). 0.2 g Na₂SO₃ was added and the mixture was boiled for half an hour.

The co-precipitate (R₂O₃) was precipitated with 20 mL NH₃ and filtered through a "Whiteband" filter, with thorough washing of the residue.

The R₂O₃ was washed back into the co-precipitation vessel and evaporated to dryness with 10 mL HNO₃ (65%). The sample was then dissolved in 15 mL HCl (37%) and 10 mL HNO₃ (65%) and evaporated to dryness.

After dissolution of the residue in 5 mL HCl (37%) and filtration through a "Whiteband" filter the solution was made up to 50 mL. This solution was then analyzed by the method of standard additions. Table 3 shows the Standard addition calibration results for Cr.

Table 3. Standard Addition Results for Cr

Sample	Conc ppm	%RSD	Mean Abs	Readings	
Blank	0.000		0.001	0.002	0.001
Standard 1	0.200	1.3	0.083	0.082	0.083
Standard 2	0.500	1.3	0.118	0.116	0.119
Standard 3	1.000	0.2	0.192	0.191	0.192
Sample	0.310	2.4	0.045	0.045	0.046

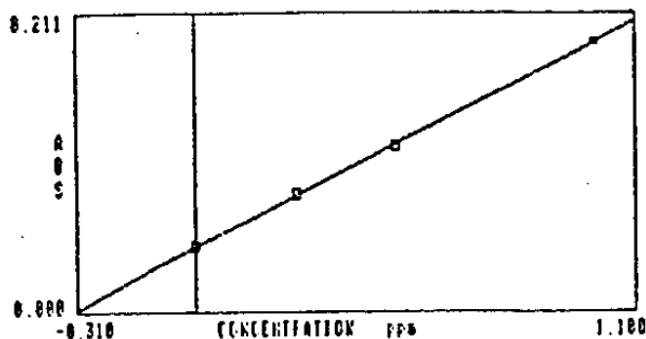


Figure 1. Calibration graph for Cr.

Direct Flame Measurements

200 mL of the caustic suspension was boiled for about half an hour with 20 mL HNO₃ (65% p.a. Merck) and about 1 mL H₂O₂ (27%), and then made up to 500 mL. A part of this sample solution was filtered through a "Whiteband" filter. This filtrate was then measured against matrix-matched standards. A reagent blank was also prepared and measured similarly.

Preparation of the test solution:

- 50 g CaCO₃ (Suprapur)
- 50 g NaCl (Suprapur)
- 60 mL HCl 7% (p.a. Merck)
- 40 mL HNO₃ 65% (Suprapur)
- 0.22 mg SO₄²⁻ (12 mL H₂SO₄ 1:100)

These reagents were made up to 1 liter with the listed heavy metals (Table 4). It should be noted that the reagents, particularly the acids, should be tested for their heavy metal content.

Table 4. Concentration of Standards for Direct Flame Measurements

	mg/L Cu	mg/L Pb	mg/L Ni	mg/L Cd
Blank	0	0	0	0
Standard 1	0.08	0.20	0.04	0.008
Standard 2	0.20	0.50	0.10	0.020
Standard 3	0.40	1.00	0.20	0.040
Standard 4	0.80	2.00	0.40	0.080

The standard values for Cu and also values for typical samples are shown in Table 5. It should be noted that 2 as the blank value is automatically subtracted from the subsequently measured values, the sample No. 4 (distilled water) shows a negative absorbance value, equivalent to approximately the value of the blank itself.

Table 5. Values of Standards and Samples for the Determination of Cu by Direct Flame Measurements

	Cu ppm	%RSD	Mean Abs	Readings		
Blank	0.000		0.007	0.008	0.007	0.007
Standard 1	0.200	6.3	0.014	0.013	0.015	0.015
Standard 2	0.50	1.1	0.036	0.036	0.037	0.036
Standard 3	1.000	1.3	0.072	0.072	0.071	0.073
Standard 4	2.000	0.9	0.146	0.145	0.147	0.147
Sample 1	0.302	2.9	0.022	0.021	0.022	0.022
Sample 2	0.369	0.2	0.027	0.027	0.037	0.027
Sample 3	0.502	1.5	0.027	0.037	0.027	0.036
Sample 4	-0.074	8.3	-0.005	-0.005	-0.006	-0.005

Direct Graphite Furnace Measurements

50 mL of the suspension was boiled for about 10 minutes with 25 mL HNO₃ (conc. p.a.) and about 1 mL H₂O₂ (30% p.a.) and then made up to 1 liter. The samples were then measured against the matrix-matched calibration standards.

The constitution of the matrix solution was as follows:

- 63 g CaCO₃ (Suprapur)/L
- 25 g NaCl (Suprapur)/L
- 75 mL HCl (30% Suprapur)/L
- 250 mL HNO₃ (65% Suprapur)/L

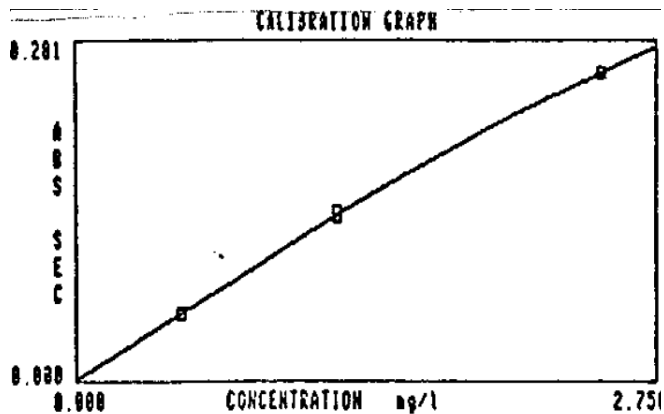


Figure 2. Calibration graph for Pb.

The matrix solution was once more diluted 1: 10 and spiked with the appropriate standards. The Pb measurements were carried out using the platform technique. The calibration data for Pb are shown in Table 6.

Table 6. Calibration Data for Pb by Graphite Furnace Atomization

Sample	Conc mg/L	%RSD	Mean Abs	Readings	
Blank	0.000		0.007	0.006	0.008
Standard 1	0.500	2.7	0.055	0.056	0.054
Standard 2	0.250	2.9	0.137	0.134	0.140
Standard 3	2.500	1.1	0.255	0.257	0.253

The atomization of Ni was made directly from the measurements graphite tube wall. The measurement values are listed in Table 7.

Table 7. Calibration Data of Ni by Graphite Furnace

Sample	Conc mg/L	%RSD	Mean Abs	Readings	
Blank	0.000		0.002	0.003	0.000
Standard 1	0.200	1.1	0.048	0.048	0.049
Standard 2	0.500	3.8	0.123	0.119	0.126
Standard 3	1.000	0.0	0.234	0.234	0.234

The program parameters are shown in Table 8.

Table 8. Instrument Parameters for Ni Analysis by Graphite Furnace

Program 1	Ni AA-98
Instrument mode	Absorbance
Calibration mode	Concentration
Measurement mode	Peak height
Lamp position	1
Lamp current (ma)	4
Slit width (nm)	0.2
Slit height	Normal
Wavelength (nm)	232.0
Sample introduction	Sampler premixed
Time constant	0.05
Measurement time (sec)	1.0
Replicates	1
Background correction	Off

Step no.	Temperature (C)	Furnace Parameters		Gas type command	Read
		Time (sec)	Gas flow (L/min)		
1	75	1.0	3.0	Normal	No
2	110	5.0	3.0	Normal	No
3	150	30.0	3.0	Normal	No
4	900	2.0	3.0	Normal	No
5	900	15.0	3.0	Normal	No
6	900	2.0	0.0	Normal	No
7	2400	0.8	0.0	Normal	Yes
8	2400	2.0	0.0	Normal	Yes
9	2400	5.0	3.0	Normal	No

	Sampler Parameters Volumes (µl)		
	Solution	Blank	Modifier
Blank	—		15
Standard1	15		
Standard 2	15		
Standard 3	15		
Sample	15		
Recalibration rate	15		
Reslope rate	5		
Multiple inject	No		
Hot inject	Yes		
Pre inject	No		
Temperature	75 °C		
Inject rate	5		

Conclusion

A comparison of the three methods:

1. Indirect flame atomization
2. Direct flame atomization
3. Graphite furnace atomization

showed that the graphite furnace technique is best suited for this type of analytical problem. The sensitivity of flame AAS was often inadequate, due to the low detection limits which had to be achieved. The indirect flame atomization method, together with pre-concentration, was accurate, but very time consuming. A comparison of the 3 methods is summarized in Table 9.

Table 9. Comparison of Results for Extraction, Direct Flame and Graphite Furnace Methods for Cd, Cu, Ni and Pb

	Sample no.	1 Extraction	2 Direct	3 GTA-96
mg Cd/L	1	0.017	0.018	0.020
	2	0.031	0.032	0.030
mg Cu/L	1	0.31	0.33	0.27
	2	0.37	0.37	0.32
mg Ni/L	1	0.29	0.22	0.23
	2	0.34	0.32	0.27
mg Pb/L	1	0.72	0.75	0.78
	2	1.13	1.21	1.21

The comparison between the indirect flame determinations(1) and the graphite furnace technique (2) for Cr is presented in Table 10.

Table 10. Comparison of Results Between Indirect Flame and Graphite Furnace Methods for Cr

	Sample no.	1 Extraction	2 GTA-96
mg Cr/L	1	0.31	0.29
	2	0.36	0.34

These investigations have shown that the values found, with the different methods, lie within the acceptable range for these trace elements.

For the individual elements, characteristic concentrations were measured in the caustic suspensions. The results are summarized in Table 11.

Table 11. Characteristic Concentrations for Graphite Furnace Technique

Element	Concentration (mg/L)	Injection volume (mL)
Cd	0.001	144
Cu	0.01	12
Ni	0.02	15
Pb	0.04	7
Cr	0.007	8

Reference

1. Abwasserabgabengesetz Bundesgesetzblatt, **1987**, Part 1, p. 881

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