Challenge

Analysis of Na, K, Mg, Co, Ni, Cu, Zn, Cd, and Pb in water and soil samples in remote regions with restricted acetylene supply.

Solution

Simple and cost-efficient analysis using a liquefied petroleum gas (LPG) flame atomic absorption spectrometer.

Simple and Cost-efficient Analysis of Easily Atomizable Elements Using LPG Flame AAS

Introduction

In remote areas of the world, it can be difficult to obtain a regular supply of acetylene gas for the operation of a flame atomic absorption spectrometer. Nevertheless, these regions face an increasing demand for elemental analysis, e.g., in environmental samples such as natural water, wastewater, or soil, or in the mining sector. For this purpose, the novAA 800 flame AAS can be equipped with a special burner that uses liquefied petroleum gas (LPG) as fuel, which is more easily available even in remote areas as it is also used for cooking, heating, or as vehicle fuel. The LPG flame has a lower temperature than the acetylene flame, therefore, only elements with a low to moderate atomization temperature can be satisfactorily analyzed. In this application note, the elements Na, K, Mg, Co, Ni, Cu, Ag, Au, Zn, Cd, and Pb were analyzed in different water and soil samples to demonstrate the possibilities and limitations of the LPG burner.

Materials and Methods

Samples and Reagents

- Drinking water sample from Jena, Germany
- River water sample from the river Saale in Jena, Germany
- Industrial wastewater sample
- Reference material BAM-U110 for contaminated soil
- Nitric acid, p. a., c(HNO_3) = 65 wt-%, ρ(HNO_3) = 1.39 g/mL
- Hydrochloric acid, p. a., c(HCl) = 32 wt-%(w/w), ρ(HCl) = 1.16 g/mL
- CsCl/$LaCl_3$ buffer (100 g/L or 10 wt-% each, 5 vol-% HCl)
- CsCl buffer (100 g/L or 10 wt-%, 5 vol-% HCl)
- Ultrapure water (R = 18.2 MΩ)

Sample preparation

Industrial wastewater, river water, and drinking water samples were diluted with 1 vol-% HNO_3 and 0.1 wt-% CsCl/$LaCl_3$ buffer in ultrapure water. Calibration standards were prepared with the same diluent.

The soil sample was prepared in a microwave digestion procedure with aqua regia. An amount of 0.5 g sample was mixed with 3 mL HNO_3 and 9 mL HCl and digested stepwise at 180 °C for 15 minutes and at 200 °C for 20 minutes. Afterwards, the solution was filled up to a final volume of 50 mL with ultrapure water. Dilutions and standards were prepared with 1 vol-% HNO_3 and 0.1 wt-% CsCl buffer in ultrapure water.

Instrumentation

A novAA 800 flame AAS was equipped with a 100 mm LPG burner and an AS-FD autosampler. Sodium and potassium were measured in both, absorption and emission mode, while all other elements were measured in absorption mode. The method parameters are shown in Table 1.

Table 1: Method parameters

Element	Wavelength [nm]	Slit [mm]	Mode	Fuel gas (LPG) flow [L/h]	Burner height [mm]
Na	589.0	0.8	Absorption	26	11
	589.0	0.8	Emission	23	14
K	766.5	1.2	Absorption	26	11
	766.5	0.2	Emission	23	15
Mg	285.2	1.2	Absorption	23	8
Co	240.7	0.3	Absorption	23	9
Ni	232.0	0.5	Absorption	26	11
Cu	324.8	1.2	Absorption	26	10
Ag	328.1	1.2	Absorption	23	10
Au	242.8	1.2	Absorption	23	10
Zn	213.9	0.8	Absorption	26	10
Cd	228.8	1.2	Absorption	26	10
Pb	283.3	1.2	Absorption	23	7

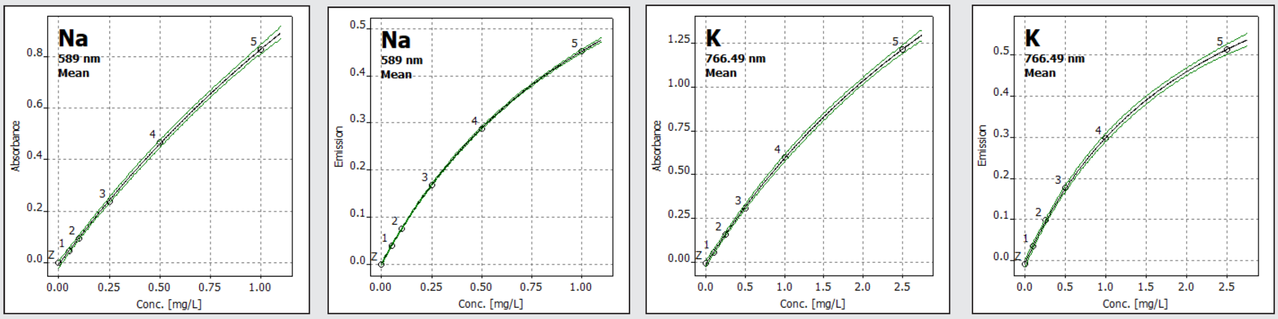
Calibration

An external calibration with aqueous standards was performed for all analytes. The concentrations of the individual standards are given in Table 2. In addition, an automax solution to adjust the wavelength in the spectrometer and to adapt the measurement sensitivity was used for the analysis of sodium (5 mg/L) and potassium (10 mg/L) in emission mode. The concentration of the automax solution should be at least as high as the highest standard; a 3-5-fold higher concentration is recommended. All calibration curves were of the non-linear rational type and are shown in Figure 2.

Table 2: Concentrations of the calibration standards

Standard	Concentration [mg/L]										
	Na	K	Mg	Co	Ni	Cu	Ag	Au	Zn	Cd	Pb
Cal 0	0	0	0	0	0	0	0	0	0	0	0
Std. 1	0.05	0.1	0.025	0.5	0.5	0.25	0.25	1	0.1	0.1	2.5
Std. 2	0.1	0.25	0.05	1	1	0.5	0.5	2.5	0.25	0.25	5
Std. 3	0.25	0.5	0.1	2.5	2.5	1	1	5	0.5	0.5	10
Std. 4	0.5	1	0.25	5	5	2.5	2.5	10	1	1	25
Std. 5	1	2.5	0.5	10	10	5	5	50	2.5	2.5	50

* AM solution = automax solution: Element standard to adjust the wavelength in the spectrometer and to adapt the measurement sensitivity in emission mode.

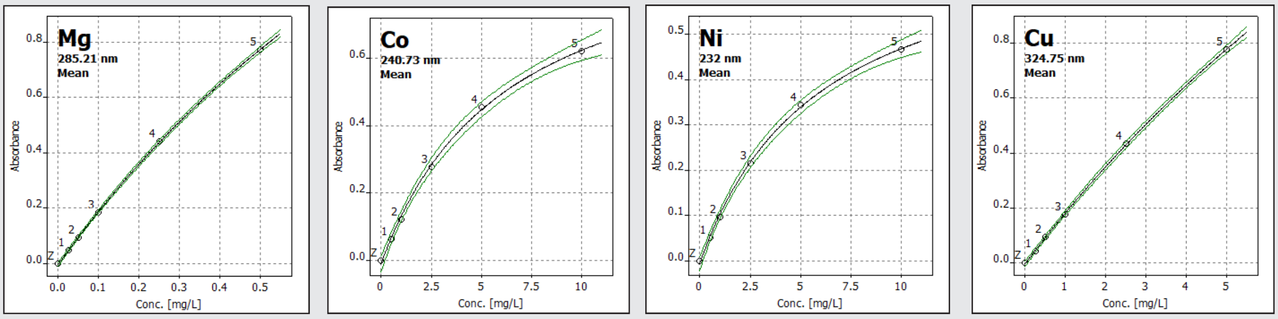


Na absorption
R^2 = 0.99993
Slope = 1.02785 Abs/mg/L
Char. conc. = 0.00424 mg/L

Na emission
R^2 = 0.99995
Slope = 0.72158 Ints/mg/L

K absorption
R^2 = 0.99992
Slope = 0.7358 Abs/mg/L
Char. conc. = 0.00579 mg/L

K emission
R^2 = 0.99976
Slope = 0.45193 Ints/mg/L



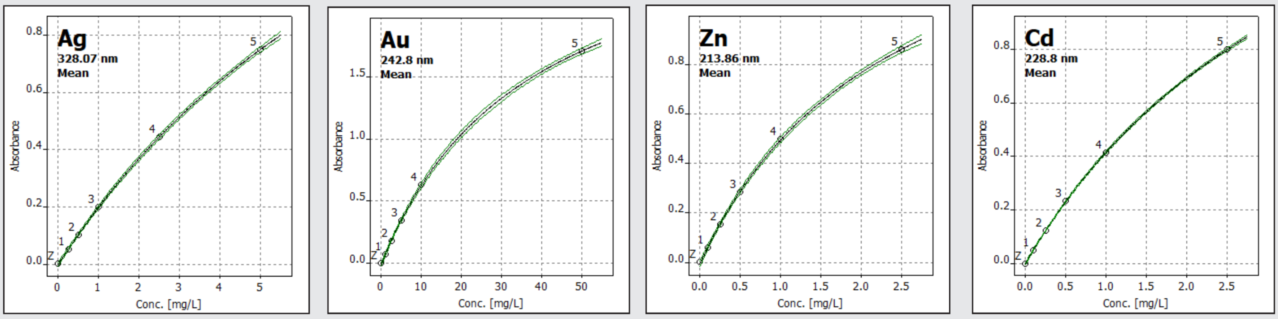
Mg absorption
R^2 = 0.99987
Slope = 1.9094 Abs/mg/L
Char. conc. = 0.00228 mg/L

Co absorption
R^2 = 0.99781
Slope = 0.16435 Abs/mg/L
Char. conc. = 0.02653 mg/L

Ni absorption
R^2 = 0.99853
Slope = 0.11818 Abs/mg/L
Char. conc. = 0.03689 mg/L

Cu absorption
R^2 = 0.99969
Slope = 0.15984 Abs/mg/L
Char. conc. = 0.02728 mg/L

Figure 2a: Calibration functions and calibration parameters. (Char. conc. = Characteristic concentration, i.e. the analyte concentration that causes an absorbance of 1%)

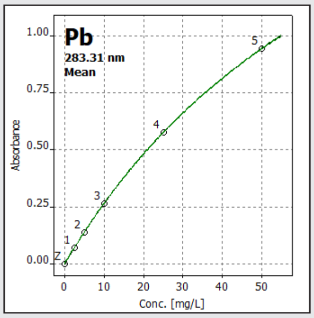


Ag absorption
R^2 = 0.99984
Slope = 0.218825 Abs/mg/L
Char. conc. = 0.01992 mg/L

Au absorption
R^2 = 0.99980
Slope = 0.08055 Abs/mg/L
Char. conc. = 0.05413 mg/L

Zn absorption
R^2 = 0.99973
Slope = 0.7091 Abs/mg/L
Char. conc. = 0.00615 mg/L

Cd absorption
R^2 = 0.99995
Slope = 0.52105 Abs/mg/L
Char. conc. = 0.00837 mg/L



Pb absorption
R^2 = 0.99999
Slope = 0.02954 Abs/mg/L
Char. conc. = 0.14762 mg/L

Figure 2b: Calibration functions and calibration parameters. (Char. conc. = Characteristic concentration, i.e. the analyte concentration that causes an absorbance of 1%)

Quality control

To examine the matrix dependency of the analysis, samples were spiked with a known analyte concentration and the recovery rate of this QC spike was determined. In addition, a certified reference material for soil was analyzed and the measured concentrations were compared with the certified concentrations.

Results and Discussion

The results of the drinking water analysis for Na, K, and Mg (Table 3) were in accordance with the concentrations given by the water supplier.[1] The recovery rates of the QC spikes, ranging from 97.5 to 101.2%, were excellent and indicate almost no matrix influence. In absorption mode, the limits of detection were lower and the results were slightly closer to the values stated by the supplier than those obtained in emission mode.

Table 3: Results for drinking water

Element	DF	Measured conc. [mg/L]	RSD [%]	Expected conc.[1] [mg/L]	Recovery rate exp. conc. [%]	Conc. QC spike [mg/L]	Recovery rate QC spike [%]	LOD [µg/L]
Na (Abs)	100	7.79	0.8	8.0	97.4	0.1	97.5	0.6
Na (Ems)	100	6.92	1.3	8.0	86.5	0.1	97.8	5.2
K (Abs)	10	3.53	3.6	3.5	100.9	0.25	99.8	8.3
K (Ems)	10	3.88	1.0	3.5	110.9	0.25	101.2	10.2
Mg	100	23.75	1.2	24.0	99.0	0.1	99.2	1.3

DF = dilution factor, RSD = relative standard deviation of three measurement replicates, LOD = limit of detection

For the river water (Table 4) and the industrial wastewater (Table 5), no certified concentrations were available. Therefore, the quality of the analysis was estimated via a recovery experiment. The recovery rates of the QC spikes for Na, K, and Mg in both sample types with values from 90.9 to 104.6% in absorption mode and 94.8 to 113.8% in emission mode show that the analysis was largely unaffected by the matrix and gave reliable results. The wastewater samples required a high dilution factor of 50,000. Alternatively, the burner head could be rotated by 90° to work with lower dilution factors.

Table 4: Results for river water from the river Saale

Element	**DF**	**Measured conc. [mg/L]**	**RSD [%]**	**Conc. QC spike [mg/L]**	**Recovery rate [%]**	**LOD [µg/L]**
Na (Abs)	500	50.13	0.5	0.1	97.0	0.6
Na (Ems)	500	48.37	0.5	0.1	94.8	5.2
K (Abs)	10	4.51	1.9	0.25	90.9	8.3
K (Ems)	10	4.87	0.5	0.25	94.9	10.2
Mg	100	10.56	1.4	0.1	99.6	1.3

DF = dilution factor, RSD = relative standard deviation of three measurement replicates, LOD = limit of detection

Table 5: Results for industrial wastewater

Element	**DF**	**Measured conc. [mg/L]**	**RSD [%]**	**Conc. QC spike [mg/L]**	**Recovery rate [%]**	**LOD [µg/L]**
Na (Abs)	50,000	5,330	1.3	0.1	98.5	0.6
Na (Ems)	50,000	5,204	1.3	0.1	101.6	5.2
K (Abs)	1,000	725.5	2.4	0.25	104.6	8.3
K (Ems)	1,000	739.1	1.4	0.25	113.8	10.2
Mg	100	7.42	1.4	0.1	101.5	1.3

DF = dilution factor, RSD = relative standard deviation of three measurement replicates, LOD = limit of detection

In Table 6 on the following page, the results for the analysis of the heavy metals Co, Ni, Cu, Ag, Au, Zn, Cd, and Pb in a certified reference material for contaminated soil are presented. For analytes without certified concentration (Ag, Au) or with certified concentrations close to the detection limit (Co, Cd, Pb), additional spike experiments were performed. The results for Cu, Ag, Au, Zn, Cd, and Pb were satisfactory with recovery rates above 80% (83.5–95.8% recovery of the certified values and 80.5–91.2% recovery of the QC spikes). The precision for these elements was very good with RSDs ranging from 0.1 to 2.1%. For Co and Ni, on the other hand, significant underdetermination occurred with recoveries in the range of 65.5 to 78.6%. These observations can be explained by the fact that Co and Ni have a higher atomization energy than the other elements and therefore require a higher flame temperature. The LPG flame with a maximum temperature of 1,900 °C does not provide enough energy to quantitatively atomize elements with a higher atomization temperature. A more detailed explanation of the technical possibilities and limitations of the LPG flame can be found in the TechNote.[2]

Table 6: Results for industrial wastewater

Element	DF	Certified conc. [mg/kg]	Measured conc. [mg/kg]	RSD sample [%]	Recovery rate CRM [%]	Spiked conc. [mg/L]	RSD spike [%]	Recovery rate spike [%]	LOD [µg/L]
Co	1	14.5	11.4	2.2	78.6	1.00	0.4	70.0	22.4
Ni	1	95.6	62.6	4.4	65.5	–	–	–	13.9
Cu	1	262	218.7	0.1	83.5	–	–	–	8.9
Ag	1	n.a.	3.4	25.2	–	1.00	2.0	91.2	13.5
Au	1	n.a.	4.07	0.1	–	5.00	0.9	86.1	21.3
Zn	50	990	945.4	1.4	95.5	–	–	–	1.4
Cd	1	7.0	6.12	3.9	87.5	0.50	0.7	80.5	2.3
Pb	1	185.0	177.2	1.1	95.8	25.0	0.8	88.3	47.9

DF = dilution factor, RSD = relative standard deviation of three measurement replicates, LOD = limit of detection

Conclusion

In remote areas, a regular supply of acetylene often cannot be ensured, while liquefied petroleum gas (LPG) is more readily available. The novAA 800 flame AAS with LPG burner provides very good results for the analysis of Na, K, and Mg in water samples and satisfactory results for the analysis of Cu, Ag, Au, Zn, Cd, and Pb in soil samples. These elements have a low to moderate atomization energy and therefore can be easily atomized by the LPG flame, which has a lower temperature than an acetylene/air flame. For analytes with a higher atomization energy, like Ni and Co, whether they can be satisfactorily analyzed with an LPG burner depends on the sample matrix. More information on the technical possibilities and limitations of the LPG flame regarding the analysis of different elements can be found in the referenced TechNote.[2] In conclusion, the novAA 800 with LPG burner is a suitable solution for elemental analysis of readily atomizable elements in remote areas where a regular supply of acetylene cannot be assured.

References

[1] Trinkwasserbeschaffenheit und eingesetzte Aufbereitungsstoffe im Versorgungsgebiet des Zweckverbandes JenaWasser, https://www.jenawasser.de/fileadmin/inhalte/3_Trinkwasser/Trinkwasserzusammensetzung.pdf, accessed December 10, 2020

[2] Analytik Jena, Flame AAS with liquefied petroleum gas (LPG); TechNote, 2021.

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