Challenge
Reliable and cost-effective heavy metal analysis in matrix-rich sewage sludges and soils.

Solution
Automated elemental analysis with the ZEEnit 700P combining flame and furnace technique for ideal suitability in the required concentration range.

Intended audience
Private and state environmental laboratories as well as wastewater treatment plants.

Standardized Heavy Metal Determination in Sewage Sludges and Soils Using Atomic Absorption Spectrometry (AAS)

Introduction

Sewage sludge is generated as a waste product of wastewater treatment and consists of organic and mineral substances in enriched form. Thus, especially plant nutrients, such as phosphate and nitrate are present in higher concentrations. Sewage sludge can be used in agriculture as a primary marterial for the fertilizer production. One of the concerns is the content of heavy metals in sewage sludge. Of concern here are heavy metals in sewage sludges, which are released into the environment, where they eventually migrate into plants and conterminating the ground water. Hence, apart from monitoring heavy metal contents in sewage sludge, their determination in soils is also a routine task.

The reuse of sewage sludge is regulated by national directives and ordinances, in Germany by the sewage sludge ordinance (AbfKlärV). The aim of the regulations is the reduction of the anthropogenic emission of contaminants into the environment to a neglectable level. For the elements lead, cadmium, chromium, copper, nickel, and zinc (sometimes also manganese and cobalt) the analysis by Atomic Absorption Spectrometry (AAS) is specified in multiple norms (e.g., DIN ISO 11047 or DIN EN ISO 15586). AAS is a simple, robust, cost effective, and well established technique used among others by wastewater treatment plants, in governmental institutions, or contract laboratories. This application note describes the analysis of sewage sludge by flame as well as graphite furnace atomic absorption spectrometry. Using the AAS ZEEnit 700P, both atomization techniques can be performed without modification. Advantages are offered by the ZEEnit series due to its Zeeman background correction with a variable magnetic field strength up to one Tesla, which can be operated in 2-field, 3-field and dynamic mode. The dynamic mode in graphite furnace technique combines the 2-field and the less sensitive 3-field mode and, therefore, automatically enables an enlarged measuring range. Samples with very high matrix loads such as sewage sludge can thus be easily analyzed with excellent background correction and without additional dilution steps.

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Materials and Methods

Heavy metal analysis by ZEEnit 700P is shown on the example of certified reference material. All operating steps as well as the purity of the reagents and used materials correspond to the guidelines of the (ultra) trace analysis.

Samples and reagents

- Concentrated HNO_3 (65%)
- Concentrated HCl (37%)
- Cesium chloride-lanthanum chloride (Cs/La) buffer solution according to Schinkel (10 g/L CsCl, 100 g/L $LaCl_3$)
- Mg-modifier (10 g/L $Mg(NO_3)_2$)
- Pd-modifier (10 g/L Pd)
- Ascorbic acid
- Certified single element standards for Cr, Mn, Co, Ni, Cu, Zn, Cd, and Pb (Concentration of the analyte respectively 1000 mg/L)
- Reference material:
  - BCR-143R sewage sludge with enriched soil (European Commission, Institute for Reference Materials and Measurements)
  - BCR-146R industrial sewage sludge (European Commission, Institute for Reference Materials and Measurements)
  - BAM-U110 contaminated soil (BAM, German federal institute of material research and testing, 2006)

Sample preparation

The samples were digested according to the DIN ISO 11466 using aqua regia. The weight of the sample material was approx. 0.3 g. The digesting solution was filled up to 50 mL with the corresponding diluent.
Sample preparation for flame measurement is based on the DIN ISO 11407. For the dilution of standards and samples even lower acid concentrations than listed in the norm stabilize the measurement solutions adequately.
For measurements by flame technique the samples were diluted with a solution containing 21 % (v/v) concentrated HCl and 7 % (v/v) concentrated HNO_3. For the elements chromium and manganese, an additional 10 % (v/v) Cs/La buffer solution was added.
The sample dilution for the measurement by graphite furnace technique is based on the DIN EN ISO 15586. The corresponding diluent was 1 % (v/v) HNO_3.

Calibration for flame technique

In accordance with the DIN ISO 11047, the calibration standards were prepared in a solution containing 21 % (v/v) HCl and 7 % (v/v) HNO_3. Such a solution with 21 % (v/v) HCl and 7 % (v/v) HNO_3 was also used as the blank value for the calibration. For the elements chromium and manganese, an additional 10 % (v/v) Cs/La buffer solution was added.
All standards were prepared from certified single element standards at a concentration of 1000 mg/L. The calibration functions for the flame technique are shown in Figures 1 to 8. The concentrations of the applied calibration standards are given in table 1.
According to the DIN ISO 11047, lead is measured at the wavelength 217 nm. Alternatively, the wavelength 283 nm is recommended. The slightly less sensitive absorption line at 283 nm provides a better signal-to-noise ratio and reduced unspecific absorption.

Table 1: Concentration of the calibration standard for flame technique

Standard	Cd [mg/L]	Co [mg/L]	Cr [mg/L]	Cu [mg/L]	Mn [mg/L]	Ni [mg/L]	Pb [mg/L]	Zn [mg/L]
Cal.-Std. 0	0	0	0	0	0	0	0	0
Cal.-Std. 1	0.2	1	1	1	0.4	1	1	0.2
Cal.-Std. 2	0.4	2	2	2	1	2	2	0.4
Cal.-Std. 3	0.8	4	4	4	2	4	4	0.8
Cal.-Std. 4	1.2	6	6	6	4	6	6	1.2
Cal.-Std. 5	1.6	8	8	8	6	8	8	1.6
Cal.-Std. 6	2.0				8			2.0

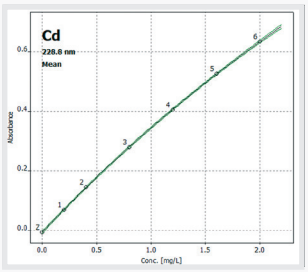

Figure 1: Cd
$R^2_{(adj)}$ = 0.9999 (non-linear)

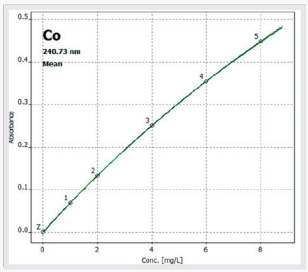

Figure 2: Co
$R^2_{(adj)}$ = 0.9999 (non-linear)

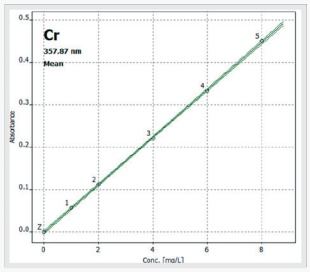

Figure 3: Cr (Acetylene/Nitrous oxide)
$R^2_{(adj)}$ = 0.9998 (linear)

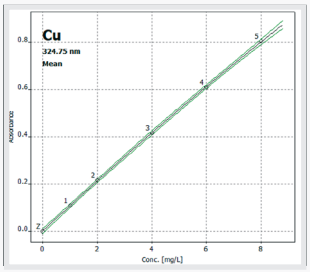

Figure 4: Cu
$R^2_{(adj)}$ = 0.9998 (non-linear)

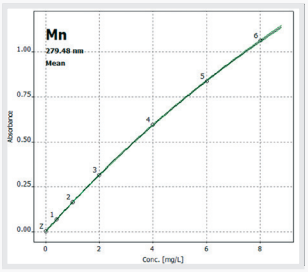

Figure 5: Mn (Acetylene/Nitrous oxide)
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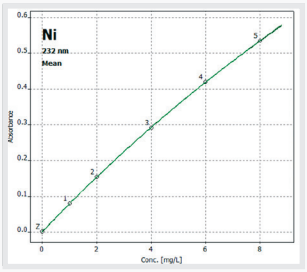

Figure 6: Ni
$R^2_{(adj)}$ = 1.000 (non-linear)

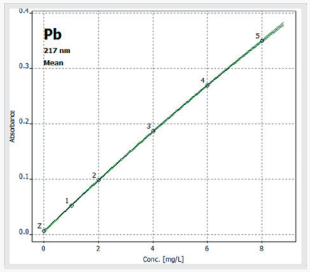

Figure 7a: Pb (217 nm)
$R^2_{(adj)}$ = 1.0000 (non-linear)

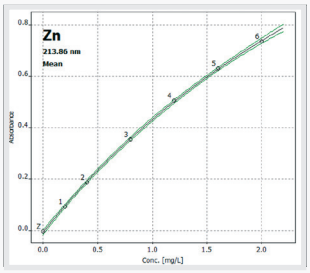

Figure 8: Zn
$R^2_{(adj)}$ = 0.9997 (non-linear)

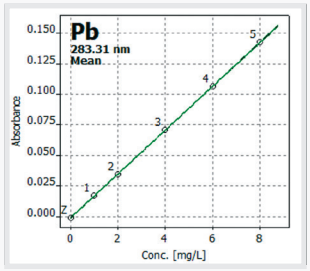

Figure 7b: Pb (283 nm)
$R^2_{(adj)}$ = 1.0000 (linear)

Calibration for graphite furnace technique

In accordance with DIN EN ISO 15586, the calibration standards were prepared as shown in table 2. The calibration standards were stabilized with diluted nitric acid (1 % (v/v) concentrated HNO_3). The diluted HNO_3 solution (1 % (v/v) HNO_3) was used as blank solution and as diluent.
A Pd-Mg solution (1 g/L Pd, 0.5 g/L $Mg(NO_3)_2$), a Mg solution (0.5 g/L $Mg(NO_3)_2$), and a solution containing $(NH_4)H_2PO_4$ (1 % (w/w)) were used as matrix modifiers.

For better stabilization of highly volatile chloride compounds of the analytes, ascorbic acid can be used in addition to the Pd/Mg solution to pre-reduce the palladium. This can be automatically injected into the graphite tube by the autosampler. As a simultaneous mixing in a sample vessel will cause the palladium to precipitate. Therefore, the autosampler is capable of a contact-free uptake of these solutions in one aspiration step. This can be programmed in the software as an option in the method parameters.

Table 2: Concentration of the calibration standards for graphite furnace technique

Standard	Cd [µg/L]	Co [µg/L]	Cr [µg/L]	Cu [µg/L]	Mn [µg/L]	Ni [µg/L]	Pb [µg/L]
Cal.-Std. 0	0	0	0	0	0	0	0
Cal.-Std. 1	0.4	6	2	3	1.5	7	1
Cal.-Std. 2	1.2	18	6	9	4.5	21	2
Cal.-Std. 3	2.0	30	10	15	7.5	35	4
Cal.-Std. 4	2.8	42	14	21	10.5	49	6
Cal.-Std. 5	4.0	60	20	30	15.0	70	8

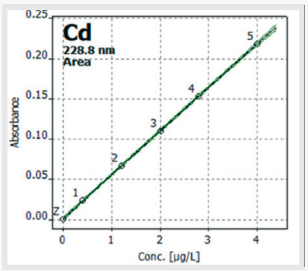

Figure 9: Cd
$R^2_{(adj)}$ = 0.9999 (linear)

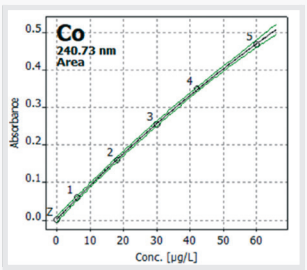

Figure 10: Co
$R^2_{(adj)}$ = 0.9995 (non-linear)

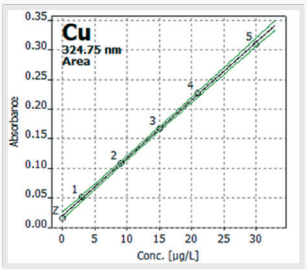

Figure 11: Cu
$R^2_{(adj)}$ = 0.9990 (linear)

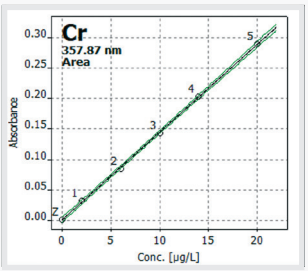

Figure 12: Cr
$R^2_{(adj)}$ = 0.9995 (linear)

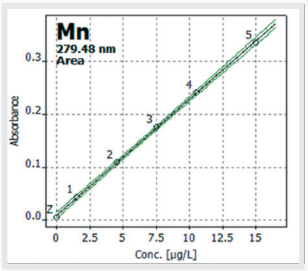

Figure 13: Mn
$R^2_{(adj)}$ = 0.9991 (linear)

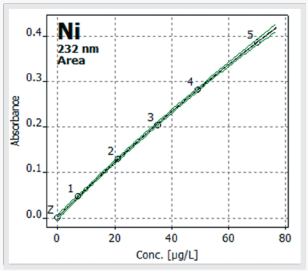

Figure 14: Ni
$R^2_{(adj)}$ = 0.9997 (non-linear)

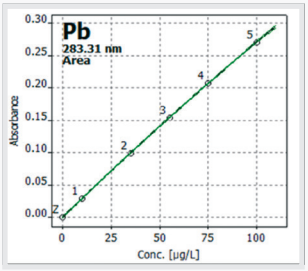

Figure 15: Pb (283 nm)
$R^2_{(adj)}$ = 0.9999 (non-linear)

Instrumentation

The analysis was performed using both flame technique and graphite furnace technique of the ZEEnit 700P. The instrument parameters are summarized in table 3 to 6. Element-specific temperature programs are used for the graphite furnace technique. These are shown in table 7.

Table 3: General instrument specification for flame technique

Parameter	Specification
Device	ZEEnit 700P
Burner type and position	50 mm, 0°
Flame type	Acetylene/air; acetylene/nitrous oxide
Rinsing solution	2 % (v/v) HCl

Table 4: Method settings for flame technique

Element	Wavelength [nm]	Slit [nm]	Lamp current [mA]	Flame type	Fuel gas flow [L/h]	Burner height [mm]	Background correction
Cd	228.8	1.2	2	Air/C_2H_2	45	4	D_2-HCL
Co	240.7	0.2	6	Air/C_2H_2	65	6	D_2-HCL
Cr	357.9	0.2	5	Air/C_2H_2 N_2O/C_2H_2	95 185	10 4	-
Cu	324.8	1.2	2	Air/C_2H_2	45	5	D_2-HCL
Mn	279.5	0.2	6	Air/C_2H_2 N_2O/C_2H_2	80 180	6 4	D_2-HCL
Ni	232.0	0.2	5	Air/C_2H_2	45	5	D_2-HCL
Pb	217.0 283.3	1.2	4	Air/C_2H_2	60	6	D_2-HCL
Zn	213.9	0.5	2	Air/C_2H_2	45	4	D_2-HCL

Table 5: General instrument specification for graphite furnace technique

Parameter	Specification
Device	ZEEnit 700P
Tube type	PIN platform
Modifier	Pd/Mg (1 g/L Pd, 0,5 g/L Mg $(NO_3)_2$) 1 % (w/w) ascorbic acid Mg (0.5 g/L Mg $(NO_3)_2$) $NH_4H_2PO_4$ (1 % (w/w))
Repeat measurements	3
Evaluation	Area
Background correction	Zeeman (1 T)
Rinsing solution	1 % (v/v) HNO_3 0.05 % (w/w) tergitol

Table 6: Method settings for graphite furnace technique

Element	Wavelength [nm]	Slit [nm]	Lamp current [mA]	Modifier	Magnetic field strength [T]
Cd	228.8	0.8	2	$NH_4H_2PO_4$	1
Co	240.7	0.2	5	Mg	1
Cr	357.9	0.2	4	Mg	0.7
Cu	324.8	0.8	2	Pd/Mg*	1
Mn	279.5	0.2	5	Pd/Mg*	1
Ni	232.0	0.2	4	Mg	1
Pb	283.3	0.8	3	$NH_4H_2PO_4$	1

* addition of ascorbic acid for Pd reduction

Table 7: Furnace program for graphite furnace technique

Element	Temp. [°C]	Ramp [°C/s]	Hold [s]
Cd	85	6	15
	95	3	15
	110	5	10
	350	50	5
	550	300	10
	1450	1400	3
	2450	500	4

Element	Temp. [°C]	Ramp [°C/s]	Hold [s]
Co	85	6	15
	95	3	15
	110	5	10
	350	50	5
	950	300	10
	2200	1500	4
	2450	500	4

Element	Temp. [°C]	Ramp [°C/s]	Hold [s]
Cu	85	6	15
	95	3	15
	110	5	10
	350	50	5
	950	300	10
	2100	1500	4
	2450	500	4

Element	Temp. [°C]	Ramp [°C/s]	Hold [s]
Mn	85	6	15
	95	3	15
	110	5	10
	350	50	5
	700	300	10
	1600	1500	4
	2450	500	4

Element	Temp. [°C]	Ramp [°C/s]	Hold [s]
Ni	85	6	15
	95	3	15
	110	5	10
	350	50	5
	1000	300	10
	2450	1500	5
	2550	500	4

Element	Temp. [°C]	Ramp [°C/s]	Hold [s]
Pb	85	6	15
	95	3	15
	110	5	10
	350	50	5
	700	300	10
	1600	1400	3
	2450	500	4

Results and Discussion

The results of heavy metal determination in the certified reference materials are shown in table 8. No or only low dilution factors were applied using the flame technique. Using the more sensitive graphite furnace technique a stronger dilution of the samples was necessary for most elements.

The quantification of chromium and manganese may show interferences with the air-acetylene flame. This can be compensated by an increased addition of Cs/La solution or by adding of $NaSO_4$ (e.g., 0.1 % (w/w)). Alternatively, analysis can be performed using a nitrous oxide-acetylene flame. With this type of flame the occurring interferences of the air-acetylene flame are hardly or not at all recognizable.

The relevant concentrations of zinc in environmental samples clearly exceed the measuring range of the graphite furnace technique. Therefore, this element is preferably quantified by means of the flame technique. With the ZEEnit series, the 3-field mode can be used to reduce the measurement sensitivity for zinc to a level where environmentally relevant issues can also be measured in the graphite furnace technique without using high dilution factors, high purified reagents, and acids.

After aqua regia digestion, the cobalt values of the reference material BCR 143R and BCR 146R were already close to the determination limit of the flame technique. Therefore, the graphite furnace technique was carried out here.

For the determination of lead in sewage sludge and soil, the absorption line at 283 nm was used. At this wavelength, background absorption is lower, which is advantageous for samples with matrix loads. In addition, better detection limits are achieved at 283 nm.

Table 8: Results for soil and sewage sludge reference material

Sample: BCR 143R		Flame mode			Graphite furnace mode		
Element	Cert. value [mg/kg]	Dilution factor	Meas. value [mg/kg]	Recovery rate [%]	Dilution factor	Meas. value [mg/kg]	Recovery rate [%]
Cr*	426 ± 12	1	437 ± 7.7	103	-	-	-
Mn*	858 ± 11	2	836.3 ± 3.4	97	500	872 ± 12	102
Co	12.3 ± 0.3	-	-	-	2	11.33 ± 1.2	92
Ni	296 ± 4	1	302.1 ± 1.1	102	100	291.4 ± 5.4	98
Cu	128 ± 7	1	131.9 ± 0.7	103	100	128.6 ± 12	100
Zn	1063 ± 16	10	1042 ± 2.4	98	-	-	-
Cd	72 ± 1.8	2	70.1 ± 0.7	97	250	70.33 ± 2.8	99
Pb	174 ± 4	1	168.2 ± 1.6	97	50	176.5 ± 1.4	101

Sample: BCR 146R		Flame mode			Graphite furnace mode		
Element	Cert. value [mg/kg]	Dilution factor	Meas. value [mg/kg]	Recovery rate [%]	Dilution factor	Meas. value [mg/kg]	Recovery rate [%]
Cr	174 ± 4	1	172.7 ± 0.1	99	100	172.6 ± 1.6	99
Mn	298 ± 9	2	285.6 ± 3.1	96	300	307.5 ± 2.5	103
Co	6.5 ± 0.4	-	-	-	2	6.20 ± 0.07	95
Ni	65 ± 3	1	61.2 ± 0.8	94	10	62.1 ± 1.0	96
Cu	831 ± 16	1	819.2 ± 1.9	99	100	821 ± 2.3	101
Zn	3040 ± 60	30	3020 ± 11	99	-	-	-
Cd	18.4 ± 0.4	2	17.91 ± 0.16	97	100	17.92 ± 0.23	97
Pb	583 ± 17	1	560.5 ± 6.4	96	100	588.7 ± 6.4	101

Sample: BAM U110		Flame mode			Graphite furnace mode		
Element	Cert. value [mg/kg]	Dilution factor	Meas. value [mg/kg]	Recovery rate [%]	Dilution factor	Meas. value [mg/kg]	Recovery rate [%]
Cr	190 ± 9	1	184.4 ± 0.7	97	-	-	-
Mn	580 ± 19	2	546.7 ± 1.2	94	400	586.2 ± 3.2	101
Co	14.5 ± 0.8	1	13.4 ± 1.1	92	3	14.27 ± 0.11	98
Ni	95.6 ± 4	1	91.7 ± 1.4	96	20	92.8 ± 0.8	97
Cu	262 ± 9	1	262.1 ± 2.5	100	100	252 ± 2.7	96
Zn	990 ± 40	10	948.2 ± 4.5	96	-	-	-
Cd	7 ± 0.4	1	6.65 ± 0.015	95	50	6.93 ± 0.24	99
Pb	185 ± 8	1	191.7 ± 3.1	103	50	185.2 ± 3.2	100

*analyzed with acetylene-nitrous oxide flame

Table 9: Detection limits for flame technology determined according to the 3σ-criterion of an 11-fold blank value measurement

Element	Wavelength [nm]	Detection limit [mg/L]
Cd	228.8	0.0040
Co	240.7	0.0070
Cr	357.9	0.014 (air-acetylene) 0.0095 (nitrous oxide-acetylene)
Cu	324.8	0.0030
Mn	279.5	0.0040 (air-acetylene) 0.0123 (nitrous oxide-acetylene)
Ni	232.0	0.0063
Pb	217.0 283.3	0.062 0.010

Table 10: Detection limits for graphite furnace technology determined according to the 3σ-criterion of an 11-fold blank value measurement

Element	Wavelength [nm]	Detection limit [µg/L]
Cd	228.8	0.0090
Co	240.7	0.24
Cr	357.9	0.060
Cu	324.8	0.11
Mn	279.5	0.044
Ni	232.0	0.41
Pb	283.3	0.30

Summary

Thanks to its double sample chamber concept the ZEEnit 700P offers the usage of flame technique as well as graphite furnace technique without conversion. As the listed measurements show, the less sensitive flame technique is already sufficient enough for the determination of heavy metal concentrations in sewage sludge and contaminated soil samples. For lower concentrations of heavy metals, the graphite furnace technique with its significantly higher detection strength is required for precise measurement results. The exemplary selected elements lead, cadmium, chromium, copper, nickel, manganese, cobalt, and zinc could be determined very reliably with both techniques in the environmentally relevant reference materials showing excellent recovery rates of 92–103%. Thanks to the powerful Zeeman background correction of the ZEEnit 700P, even very low levels of toxic elements such as lead and cadmium can be easily and reliably quantified even in samples with high matrix loads.
To simplify analysis procedures in routine operations, autosamplers autosamplers with an automatic standard preparation and sample dilution function are available for both flame technique and graphite furnace technique to automate the analysis procedure.

Figure 16: ZEEnit 700P with autosampler

Overview of devices and consumables

Table 11: Required devices, accessories, and consumables

Article	Article number	Description
ZEEnit 700P	813-0700P-2-K	Flame- and graphite furnace AAS with Zeeman background correction with furnace vision tool
AS-GF Autosampler	-	Autosampler with auto-dilution for graphite furnace, included in the system
Chiller	810-60053-0	Software-controlled cooling system for graphite furnace technique, 50 Hz (60 Hz on request)
Consumable Set G	810-60079-0	Consumables for graphite furnace ZEEnit
AS-FD	810-60501-0	Autosampler with auto-dilution for flame
Air compressor	810-60055-0	To supply AAS with water- and oil-free compressed air, 50 Hz (60Hz on request)
50 mm Burner head	810-60057-0	Burner head for acetylene/nitrous-oxide or acetylene/air flame (100 mm burner head on request)
Scraper	810-60127-0	Automatic cleaning tool for 50 mm burner head
Consumable set F	810-60258-0	Consumables for flame of novAA/contrAA/ZEEnit-series
HCL Cd	480-450.008C	Coded hollow cathode lamp Cadmium
HCL Co	480-450.013C	Coded hollow cathode lamp Cobalt
HCL Cr	480-450.012C	Coded hollow cathode lamp Chromium
HCL Cu	480-450.014C	Coded hollow cathode lamp Copper
HCL Mn	480-450.032C	Coded hollow cathode lamp Manganese
HCL Ni	480-450.036C	Coded hollow cathode lamp Nickel
HCL Pb	480-450.028C	Coded hollow cathode lamp Lead
HCL Zn	480-450.067C	Coded hollow cathode lamp Zinc

Further HCL on request

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