



### Challenge

The simple and cost-effective quantification of metals in the matrix edible oils without digestion of the samples.

### Solution

The quantification of iron, nickel, copper, arsenic, cadmium, and lead in organic matrix using GF-AAS with Zeeman background correction and dynamic mode on the ZEEnit 650P.

### Intended audience

Laboratories of the edible oil industry and contract laboratories for food products

## Quantification of Iron, Nickel, Copper, Arsenic, Cadmium, and Lead in Edible Oils Using GF-AAS

### Introduction

Edible oils are essential components of the human diet and play a crucial role in the culinary world. Not only do they serve as important sources of energy, but they also make a significant contribution to the flavor development of dishes. In addition to their flavor and nutritional importance, edible oils also contain various chemical components, including metals, which play a key role in the quality and safety of these products. The determination of metals in edible oils is therefore important, both from a health and in-process point of view. Metals in edible oils can come from a variety of sources, including the soil in which the oil crops are grown, the processing techniques used, and the storage conditions. Although some metals, such as iron, are essential to the human body, others, such as lead, cadmium, or arsenic, are toxic and can cause serious health problems at certain levels in foods. Therefore, accurate analysis and monitoring of metal content in edible oils are of utmost importance to ensure that they comply with regulatory requirements and

are safe for consumption. Process-relevant metal contents of edible oils are also crucial to determine. Even traces of metals, which, for example, act as catalyst poisons or have a significant effect on the quality or shelf life of the products, need to be detected early in the process so that further reprocessing steps can be carried out if necessary. In this application note, we will address the procedure of metal analysis in the challenging matrix of edible oils to ensure the quality and safety of these products.

Samples can be robustly and cost-effectively quantified for their metal content using atomic absorption spectrometry (AAS). Graphite furnace AAS (GF-AAS) offers high detection strength with low sample consumption. An ideal measuring instrument for this application are the spectrometers of the ZEEnit series ZEEnit 650P and ZEEnit 700P.

By pyrolyzing the sample carbon components of the matrix as well as other highly volatile components of the sample can be removed prior to the measurement step. This procedure eliminates the need for digestion of edible oils and fats. The Zeeman background correction of the ZEE nit series allows reliable quantification of low analyte contents despite a high background signal.

In addition, the variable magnetic field strength can be used to attenuate the measurement signal and, in combination with the dynamic mode, the calibration range can be significantly increased. To demonstrate the performance of the AA spectrometers of the ZEE nit series, the analytes Fe, Ni, Cu, As, Cd, and Pb were determined in common edible oils and fats.

## Materials and Methods

### Samples and reagents

- Edible Oils:
  - Rice bran oil
  - Rapeseed oil
  - Peanut oil (roasted)
  - Virgin olive oil
  - Palm oil
  - Treated coconut oil
  - Crude coconut oil
- PremiSolv (Conostan)
- 2-Propanol ( $\geq 99.5\%$ , Ph. Eur., pure)
- Ethanol (96%, Ph. Eur., pure)
- Pd-Matrixmodifier (PD 10 g L<sup>-1</sup>)
- Mg-Matrixmodifier (10 g Mg(NO<sub>3</sub>)<sub>2</sub>)
- Ascorbic acid (p.a.)
- Oil based standard (S21+K, 10 ppm, Conostan)
- Oil based standard (As, 100 ppm, Conostan)

### Sample preparation

For the density adaptation of the edible oil samples with respect to the calibration standards used, the samples are dissolved in Conostan's PremiSolv solvent. Alternatively, kerosene can be used as a solvent, in which case the furnace program should be adapted with regard to the evaporation temperature of kerosene (by inserting a drying step at approx. 250 °C). Highly viscous fats or oils such as palm oil still show a different appearance compared to the standard solutions at a dilution factor of 5, which indicates a matrix influence of the sample solution compared to the oil standards. This effect does not occur with a dilution ratio of approx. 1:20 for palm oil. With the GF-AAS sample introduction, even viscous solutions can be handled by pipetting. If the diluted samples or undiluted edible oils still show significant density differences with respect to the standards used, a matrix adapted calibration, or the method of addition (addition calibration) should be used to increase the accuracy of the measurement. Alternatively, a higher dilution of edible oils/fats with the diluent used can be performed. This will result in a density match between samples and standards.

### Calibration

The oil-based element standards were dissolved in the solvent PremiSolv from Conostan. If kerosene is used as a solvent, the furnace program should be adjusted to its evaporation temperature (insert drying step at approx. 250 °C). The dilution series was prepared on a gravimetric basis. For this purpose, oil standard was weighed in according to the desired concentration and adjusted to the corresponding total mass with PremiSolv.

A calibration series with four and five concentrations, respectively, was used to quantify the elements Ni, Cu, As, Cd, and Pb. Since the content of iron, due to the ubiquitous presence of this metal, shows a high variance in edible oils, the dynamic mode was used for the quantification. This enables a significant extension of the calibration range without causing saturation of the measurement signals. By using an average magnetic flux density, the absorption signal of the analyte is not completely separated from the baseline, but partially split. This results in an attenuation of the signal (3-field mode, 3-FM for short). In combination with the strong 2-field mode (2-FM for short), the calibration range of the GF-AAS can be significantly increased without compromising the detection limit of the method. The combination of 2- and 3-field mode is called dynamic mode.

Table 1 shows the calibration concentrations used, and figures 1–6 shows typical calibration function curves. A solution with 50  $\mu\text{g kg}^{-1}$  was used as a stock standard for nickel, copper and lead. A solution with 10  $\mu\text{g kg}^{-1}$  was used for cadmium and one with 100  $\mu\text{g kg}^{-1}$  for arsenic. For the determination of iron, two stock standards were prepared, 50  $\mu\text{g kg}^{-1}$  for the calibration function in the low concentration range (L curve, 2-FM) and 500  $\mu\text{g kg}^{-1}$  for the high standards (H curve, 3-FM).

Table 1: Standards used for calibration

Standard	Concentration [ $\mu\text{g kg}^{-1}$ ]					
	Fe	Ni	Cu	As	Cd	Pb
Stock solution 1	50	50	50	100	10	50
Stock solution 2	500					
Cal 0	0	0	0	0	0	0
Std. 1	5	5	5	25	1	5
Std. 2	12.5	12.5	12.5	50	2.5	12.5
Std. 3	25	25	25	75	5	25
Std. 4	37.5	37.5	37.5	100	7.5	37.5
Std. 5	50	50	50		10	50
Std. 6	75					
Std. 7	125					
Std. 8	250					
Std. 9	375					
Std. 10	500					

Figures 1-6: Typical calibration functions

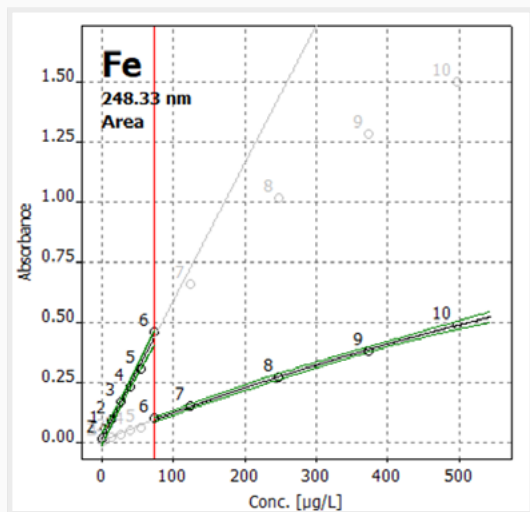


Figure 1: Fe  
 $R^2_{(adj)} = 0.998$  (L-curve 2-FM)  
 $R^2_{(adj)} = 0.9990$  (H-curve 3-FM)

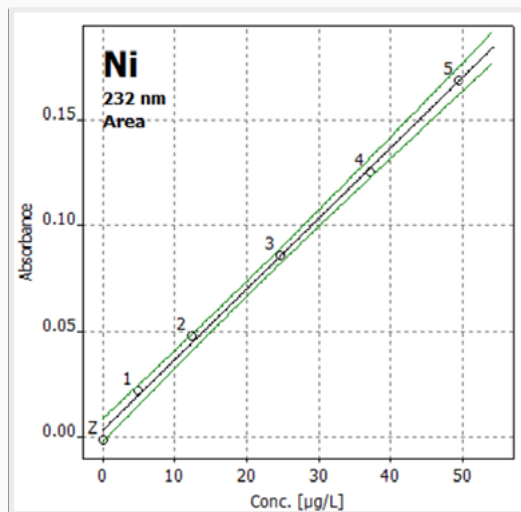


Figure 2: Ni  
 $R^2_{(adj)} = 0.997$

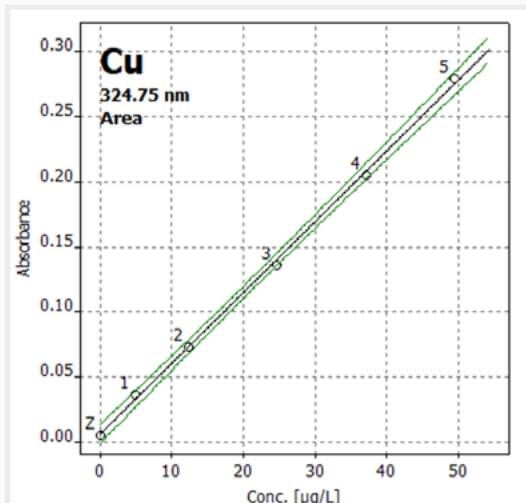


Figure 3: Cu  
 $R^2_{(adj)} = 0.9990$

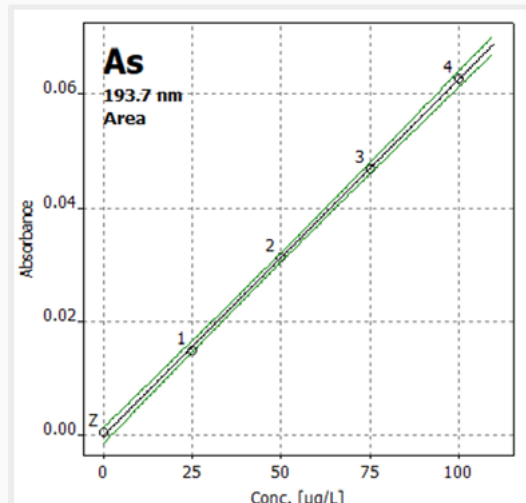


Figure 4: As  
 $R^2_{(adj)} = 0.9993$

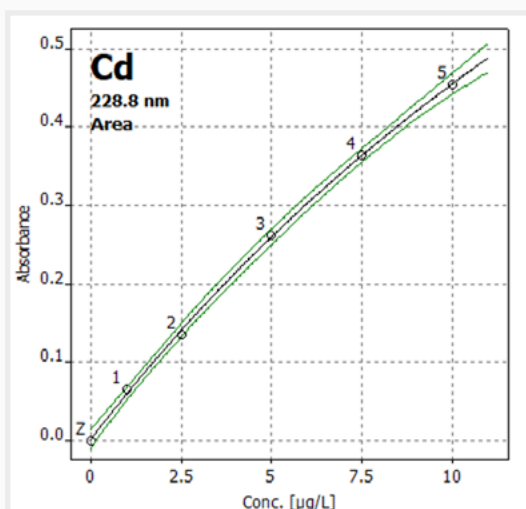


Figure 5: Cd  
 $R^2_{(adj)} = 0.9991$

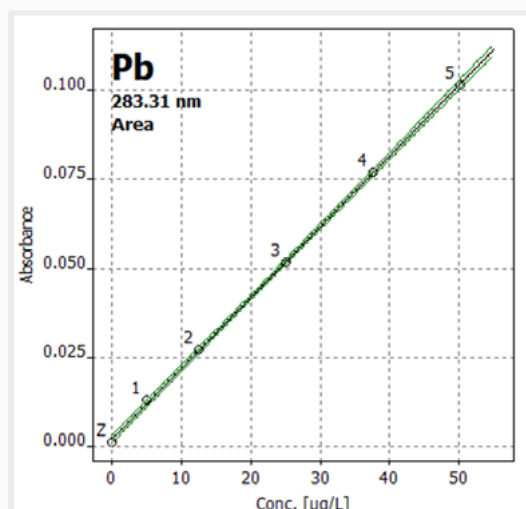


Figure 6: Pb  
 $R^2_{(adj)} = 0.9997$

### Instrument settings

The device specifications used are listed in table 2. Table 3 shows the optical parameters and table 4–9 show the respective furnace programs used.

To prepare the modifier solution used, 10% (v/v) of the Pd stock solution or 5% (v/v) Mg stock solution is added and filled up to the desired final volume with 2-propanol (application example: Add 1 mL Pd modifier stock solution or 0.5 mL Mg modifier stock solution, fill up to 10 mL total volume with 2-propanol). To chemically reduce the palladium prior to measurement, a 1% ascorbic acid solution was used. For this purpose, 1% (w/w) ascorbic acid were dissolved in ethanol (application example: 500 mg ascorbic acid is dissolved in 50 g ethanol).

For faster dissolution of ascorbic acid in ethanol, the use of an ultrasonic bath or vortex mixer is recommended. To avoid premature precipitation of the palladium(II) from the modifier solution in the tubing, the palladium-containing and ascorbic acid-containing solutions can be aspirated separately in the tubing, separated by the sample solution. This pipetting option is a selectable method setting. For the analytes iron and nickel, the magnesium-based modifier solution was used. For the quantification of copper, arsenic, cadmium, and lead, palladium was used as a modifier.

An air ashing step has been established in the furnace program. With this procedure, the fuming process of the oil samples is much more effective, and less aerosol is present than without the introduction of air. Even without oxygen, the samples in the graphite furnace can be treated in the pyrolysis step efficiently. However, without this step, more pyrolysis aerosols are produced and therefore the holding time of the pyrolysis step at 550 °C should be extended.

Table 2: Instrument specifications used

Parameter	Specification
Type of device	ZEEnit 650P
Tube type	PIN-platform
Repetitions	3
Injected volume	Standards/sample 20 µL
Evaluation	area
Modifier	Fe, Ni: Mg(NO <sub>3</sub> ) <sub>2</sub> (0.5 g L <sup>-1</sup> ) Cu, As, Cd, Pb: Pd (1 g L <sup>-1</sup> ) + ascorbic acid (10 g kg <sup>-1</sup> )
Background correction	Zeeman 1.0 T, 3-FM 0.45 T (Fe)
Rinsing solution	Kerosene

### Method parameters

Table 3: Optical setup

Element	Wavelength [nm]	Slit width [nm]	HCL current [mA]
Fe	248.8	0.2	5
Ni	232.2	0.2	4
Cu	324.8	0.8	2
As	193.7	0.8	5.5
Cd	228.8	0.8	2
Pb	283.3	0.8	3

Table 4: Furnace program used for Fe

Temperature [°C]	Ramp [°C s <sup>-1</sup> ]	Hold [s]	Level of gas flow	Gas type in the tube
90	3	10	Max	Argon
95	3	5	Max	Argon
125	3	7	Max	Argon
150	4	42	Max	Argon
550	50	20	Min/Max	Argon/Air
550	0	16	Max	Argon
950	200	7	Max	Argon
2500	1450	5	-	No gas
2550	500	4	Max	Argon

Table 5: Furnace program used for Ni

Temperature [°C]	Ramp [°C s <sup>-1</sup> ]	Hold [s]	Level of gas flow	Gas type in the tube
90	3	10	Max	Argon
95	3	5	Max	Argon
125	3	7	Max	Argon
150	4	42	Max	Argon
550	50	20	Min/Max	Argon/Air
550	0	16	Max	Argon
950	200	7	Max	Argon
2450	1450	4	-	No gas
2550	500	4	Max	Argon

Table 6: Furnace program used for Cu

Temperature [°C]	Ramp [°C s <sup>-1</sup> ]	Hold [s]	Level of gas flow	Gas type in the tube
90	3	10	Max	Argon
95	3	5	Max	Argon
125	3	7	Max	Argon
150	4	42	Max	Argon
550	50	20	Min/Max	Argon/Air
550	0	16	Max	Argon
950	200	7	Max	Argon
2450	1450	3	-	No gas
2550	500	4	Max	Argon

Table 7: Furnace program used for As

Temperature [°C]	Ramp [°C s <sup>-1</sup> ]	Hold [s]	Level of gas flow	Gas type in the tube
90	3	10	Max	Argon
95	3	5	Max	Argon
125	3	7	Max	Argon
150	4	42	Max	Argon
550	50	20	Min/Max	Argon/Air
550	0	16	Max	Argon
850	200	7	Max	Argon
2450	1450	3	-	No gas
2550	500	4	Max	Argon

Table 8: Furnace program used for Cd

Temperature [°C]	Ramp [°C s <sup>-1</sup> ]	Hold [s]	Level of gas flow	Gas type in the tube
90	3	10	Max	Argon
95	3	5	Max	Argon
125	3	7	Max	Argon
150	4	42	Max	Argon
550	50	20	Min/Max	Argon/Air
575	25	16	Max	Argon
1950	1600	3	-	No gas
2500	500	4	Max	Argon

Table 9: Furnace program used for Pb

Temperature [°C]	Ramp [°C s <sup>-1</sup> ]	Hold [s]	Level of gas flow	Gas type in the tube
90	3	10	Max	Argon
95	3	5	Max	Argon
125	3	7	Max	Argon
150	4	42	Max	Argon
550	50	20	Min/Max	Argon/Air
550	0	16	Max	Argon
750	200	7	Max	Argon
1950	1450	3	-	No gas
2500	500	4	Max	Argon

## Results and Discussion

The elements Fe, Ni, Cu, As, Cd, and Pb have been measured in common edible oil samples. The results of the measurement series are shown in table 10. Using a dilution factor (DF) of 5, recovery rates (RR) for spiked samples were determined to be between 87 to 109%. This shows that no relevant matrix influences are to be expected for the measurements. However, semi-crystalline samples, such as palm oil, still shows matrix influences for some analytes, e.g. As at a DF of 5 (RR 78%). Here, further dilution is advisable (DF 20).

Table 11 lists the typically achievable detection and quantification limits of the instrument. The method-specific detection and quantification limits consider a DF of 5. The limits are determined by the blank value method, in which an 11-fold blank value measurement was conducted and the 3 $\sigma$  or 9 $\sigma$  standard deviation criterion was used.

Table 10: Results of the quantification of Fe, Ni, Cu, As, Cd and Pb in edible oils

Sample	Dilution factor	Element	Recovery rate spike [%]	Element content in the original sample [ $\mu\text{g kg}^{-1}$ ] (standard deviation)
Rice bran oil	5	Fe	89	< LOD
		Ni	104	< LOD
		Cu	87	10.5 $\pm 0.87$
		As	92	< LOD
		Cd	107	< LOD
		Pb	108	< LOD
Rapeseed oil	5	Fe	105	38.3 $\pm 1.2$
		Ni	109	< LOD
		Cu	88	< LOD
		As	94	< LOD
		Cd	109	< LOD
		Pb	104	< LOD
Peanut oil (roasted)	5	Fe	103	259
		Ni	100	< LOD
		Cu	93	3.6 $\pm 0.32$
		As	88	< LOD
		Cd	106	< LOD
		Pb	101	< LOD
Virgin olive oil	5	Fe	95	26.5 $\pm 0.71$
		Ni	91	< LOD
		Cu	102	< LOD
		As	101	< LOD
		Cd	102	< LOD
		Pb	98	< LOD
Palm oil	20	Fe	100	6481 $\pm 326$
		Ni	87	< LOD
	5	Cu	103	91.5 $\pm 2.1$
		As	78	< LOD
	20		103	< LOD
		Cd	102	< LOD
5	Pb	107	6.8 $\pm 1.6$	

Treated coconut oil	5	Fe	101	245.0	$\pm 2.4$
		Ni	102	< LOD	
		Cu	97	< LOD	
		As	96	< LOD	
		Cd	104	< LOD	
		Pb	96	< LOD	
Crude coconut oil	5	Fe	101	951	$\pm 1.6$
		Ni	103	< LOD	
		Cu	92	8.6	$\pm 1.6$
		As	101	< LOD	
		Cd	96	< LOD	
		Pb	104	4.1	$\pm 1.6$

LOD: Limit of detection

Table 11: Limit of detection and limit of quantification determined according to the  $3\sigma$  and  $9\sigma$  criterion

Element	LOD <sub>inst</sub> [ $\mu\text{g kg}^{-1}$ ]	LOQ <sub>inst</sub> [ $\mu\text{g kg}^{-1}$ ]	LOD <sub>meth</sub> [ $\mu\text{g kg}^{-1}$ ]	LOQ <sub>meth</sub> [ $\mu\text{g kg}^{-1}$ ]
Fe	1.1	3.3	5.5	16.5
Ni	1.8	5.4	9	27
Cu	0.35	1.05	1.8	5.4
As	2.9	8.7	14.5	43.5
Cd	0.048	0.144	0.24	0.72
Pb	0.45	1.35	2.3	6.9

LOD<sub>inst</sub>/LOQ<sub>inst</sub>: Limit of detection/ limit of quantification of the instrument

LOD<sub>meth</sub>/LOQ<sub>meth</sub>: Limit of detection/ limit of quantification of the method using a typical sample dilution factor of 5



Figures 7–12: Typical signal plots of the measurement

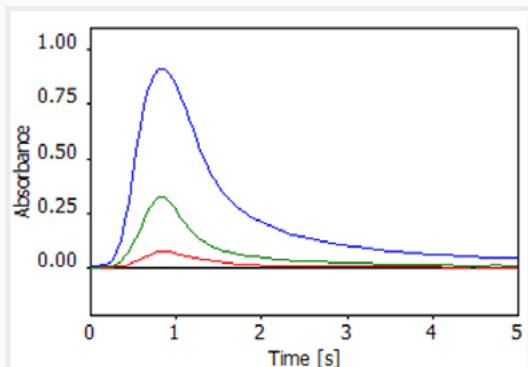


Figure 7: Fe (Sample „Palm oil“ dilution factor 20)

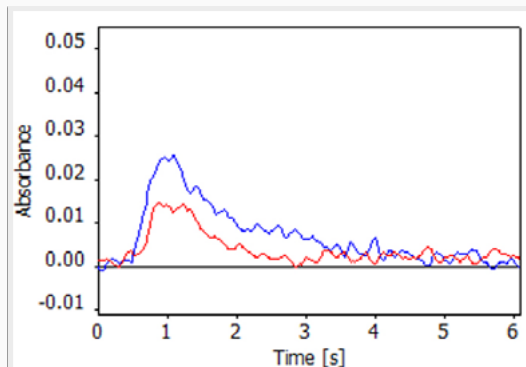


Figure 8: Ni (Sample „Palm oil“ dilution factor 5, spiked with 12.5 µg kg⁻¹ Ni)

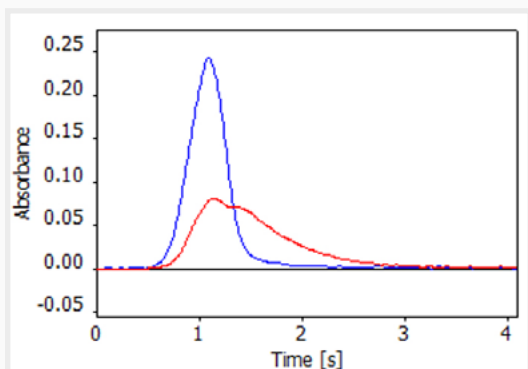


Figure 9: Cu (Sample „Palm oil“ dilution factor 5)

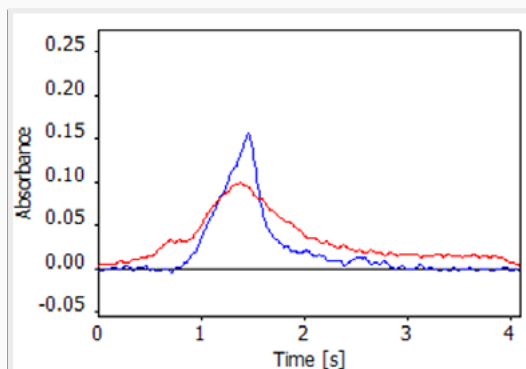


Figure 10: As (Sample „Palm oil“ dilution factor 5, spiked with 100 µg kg⁻¹ As)

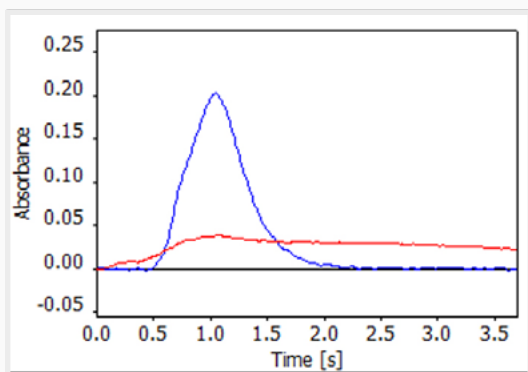


Figure 11: Cd (Sample „Palm oil“ dilution factor 5, spiked with 2.5 µg kg⁻¹ Cd)

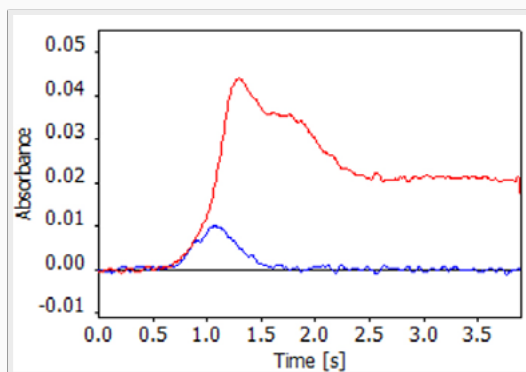


Figure 12: Pb (Sample „Palm oil“ dilution factor 5)

Red: Background signal  
 Blue: Atomic absorption signal (2-field mode)  
 Green: Atomic absorption signal (3-field mode)

## Summary

The cost-effective, robust, and highly sensitive quantification technique GF-AAS is an excellent instrument to be able to determine the heavy metal contents in common edible oil samples. With the powerful Zeeman background correction with a maximum field strength of 1 Tesla and the 3rd generation furnace, designed according to the STPF concept, the AA spectrometers of the ZEE nit series offer a stable and user-friendly measurement technique. In addition, the variable magnetic field in 3-field mode or by combining 2- and 3-field mode (dynamic mode) allows to significantly increase the calibration range of the measurement. Therefore, automatic measurement of even ubiquitous elements such as iron without high dilution of the sample becomes possible.



Figure 13: ZEE nit 650P

## Recommended device configuration

Table 12: Overview of required devices, accessories, and consumables

Article	Article number	Description
AAS – ZEE nit 650P	813-0650P-2	Graphite furnace AAS with Zeeman background correction
Graphite tubes	407-152.314	Z-graphite tube PIN-platform – pyrolytically coated
Hollow cathode lamp	Fe-HCL 480-450.026C	Coded hollow cathode lamp for the element Fe
Hollow cathode lamp	Ni-HCL 480-450.036C	Coded hollow cathode lamp for the element Ni
Hollow cathode lamp	Cu-HCL 480-450.014C	Coded hollow cathode lamp for the element Cu
Hollow cathode lamp	As-HCL 480-450.003C	Coded hollow cathode lamp for the element As
Hollow cathode lamp	Pb-HCL 480-450.028C	Coded hollow cathode lamp for the element Pb

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