

Zeitschrift: Mitteilungen aus dem Gebiete der Lebensmitteluntersuchung und Hygiene = Travaux de chimie alimentaire et d'hygiène
Herausgeber: Bundesamt für Gesundheit
Band: 73 (1982)
Heft: 1

Artikel: Nickel determination in plants and sewage sludges
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DOI: <https://doi.org/10.5169/seals-983443>

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Nickel Determination in Plants and Sewage Sludges*

Introduction

The yearly production of liquid sewage sludge in Switzerland amounts to $2-3 \times 10^6$ m³, of which 80–90% are used as fertilizers in agriculture.

Disadvantage: There is an enrichment of toxic metals in soils and plants.

Concentration of nickel in dried sewage sludges: (Investigation on 103 sewage sludges in 1978)

Range 4–1330 mg/kg

Median 52 mg/kg

Tolerance limit 200 mg/kg

Average concentration of nickel in plants: < 3 mg/kg dry matter.

Exception: Leguminous plants, which can have up to 6 mg Ni/kg dry matter.

Nickel is greatly phytotoxic.

Nickel is normally determined in sludges by atomic absorption spectrometry. The lack of standard plant (< 1 mg Ni/kg dry matter) and sludge reference material implies the use of another independent analytical method, in order to establish the accuracy of the method. The aim of this work was to choose an exact and routine method to determine nickel in plants and sewage sludges.

Experimental

Preparation of the samples

Sewage sludges

5 g wet or 100 ml liquid sludge are dried and then mineralized at 500 °C for 1–3 h.

The ashes are solubilized by boiling for 20 min in 10 ml concentrated HCl (D 1.18). After cooling, the solution is diluted to 500 ml.

Plants

5 g of dried material are mineralized at 540 °C for 3 h.

The ashes are solubilized by boiling for 5 min in 5 ml concentrated HCl (D 1.125). After cooling, the solution is diluted to 50 ml.

The nickel content of the material is determined from these solutions (table 3).

* Presented as poster.

Results

Test of the accuracy and precision of the method

Sewage sludges

The day-to-day precision and accuracy of the AAS-measurements were tested by comparison with the results of the colorimetric method on 3 different sewage sludge solutions (table 1).

Table 1. Accuracy and day-to-day precision

Samples	<i>N</i>	Flame-AAS ($\mu\text{g Ni/ml}$) $\bar{x} \pm 1s$	<i>RSD</i> %	<i>N</i>	Colorimetry ($\mu\text{g Ni/ml}$) $\bar{x} \pm 1s$	<i>RSD</i> %
Sewage sludge A	10	0.82 ± 0.04	4.6	10	0.83 ± 0.02	1.8
Sewage sludge B	10	2.70 ± 0.06	2.3	10	2.72 ± 0.04	1.7
Sewage sludge C	10	3.88 ± 0.11	2.8	10	3.84 ± 0.09	2.4

N = Number of determinations

RSD = Relative Standard Deviation

Plant material

Because of the low concentrations of nickel in plant material, it was found impossible to use direct AAS. As a result, the ETA/AAS method, preceded by extraction of the nickel content of the sample, was chosen as test method (table 2).

The deuterium background compensation was used for these measurements.

Table 2. Precision of the extraction and electrothermal atomization-AAS procedure

Samples	<i>N</i>	mg Ni/kg dry matter	<i>RSD</i> %
Grass D	11	2.38 ± 0.07	3.12
Grass E	11	2.22 ± 0.06	2.57
Grass F	11	0.96 ± 0.02	2.48

The measurements which follow were made on the same plant solutions, and in the case of the extractions the same extract was measured with the different methods (table 4). The colorimetric method showed the greatest variations for absorbance below 0.1 (= $0.08 \mu\text{g Ni/ml}$).

Table 3. Extraction and measurements

	AAS Flame	Extraction-AAS Flame	Extraction-ETA/AAS* Graphite tube	Extraction-Colorimetry
<i>Working range and concentrations</i>				
Working range ($\mu\text{g Ni}$)		0.5–5	0.25–5	1 –25
Working concentrations ($\mu\text{g Ni/ml}$)	0.5–15	0.1–1.0	0.05–1.0	0.04– 1.0
<i>Extraction</i>		Addition of HCl (2.5% v/v) to a volume of 40 ml + 10 ml of a sodium citrate solution (20% w/v) + 5 ml of a hydroxylamine hydrochloride solution (10% w/v) + 2 ml of an ethanolic dimethylglyoxime solution (1% w/v) + 3 drops of phenolphtalein solution (1% w/v) Addition of ammonia solution (25% w/w) to the colour change + H ₂ O to a final volume of 60 ml + 5 ml of a mixture of m-Xylene/MIBK (70/30) Extract by shaking for 2 min Separate the phases		pH of the resulting solution 4.6 4.4 ~ 9.0 + 20 ml of CHCl ₃ Extract once by shaking for 2 min Wash the organic phase twice with 10 ml of diluted ammonia solution (1:200) by shaking for 2 min Extract the organic phase once with 15 ml HCl (0.5 N) Separate the phases

Measurement	Aspirate organic extract in the flame		Injection: 20 μ l of organic extract		+ 2 ml of NaOH (3N) pH 1.1 + 2 ml of dimethylglyoxime (2.5% w/v in NaOH IN) pH 11.4 + 2 ml of NaOH (3N) pH 13.2 + 0.3 ml of (NH ₄) ₂ S ₂ O ₈ solution (10% w/v) + addition of distilled water to a final volume of 25 ml
Flame: C ₂ H ₂ /Air; oxidizing			Drying: 10 s 133 °C		
1 slit burner			Calcination: 15 s 600 °C		
The deuterium compensation was used in all measurements			Atomization: 20 s 2660 °C		The colour develops within 3 hours and remains stable for at least 3 days
Wavelength (nm)	232.0	232.0	232.0		465
Slit (nm)	0.2	0.2	0.2		Cell length: 4 cm
Range of linearity (μ g Ni/ml)	up to 5.0	up to 2.0	without deuterium compensation	with deuterium compensation	
Sensitivity** (μ g Ni/ml)	0.2	0.05	0.6	0.6	At least up to 1.0
Detection limit (μ g Ni/ml)	0.2	0.06	0.02	0.03	
			0.04	0.08	

* ETA/AAS = Electrothermal atomization / Atomic absorption spectrometry

** for 0.0044 Absorbance unit.

Table 4. Comparison of accuracy and day-to-day

Samples	Extraction-AAS			Extraction-ETA/AAS		
				without background compensation		
	<i>N</i>	$\bar{x} \pm 1s$	<i>RSD%</i>	<i>N</i>	$\bar{x} \pm 1s$	<i>RSD%</i>
Grass	8	0.193 ± 0.012	6.4	6	0.189 ± 0.005	2.8
Barley corn	7	0.019 ± 0.008	42.6	6	0.017 ± 0.002	14.0
Barley straw	7	0.024 ± 0.003	13.3	8	0.025 ± 0.002	8.4
Winter wheat	8	0.036 ± 0.007	20.6	6	0.036 ± 0.002	4.6
Maize corn	5	0.036 ± 0.011	29.6	5	0.037 ± 0.004	10.7

\bar{x} = Ni content in mg/kg dry matter

To control the accuracy of the colorimetric and ETA/AAS methods five samples were analysed by nondestructive neutron activation analysis and the results compared to the previous ones (table 5).

Table 5. Accuracy; comparison of colorimetry and ETA/AAS to neutron activation analysis

Samples	*** Neutron activation	Extraction-ETA/AAS	Colorimetry
	mg Ni/kg dry matter		
* Leaves of...			
Codia	186	175	171
Eucalyptus	3.2	3.1	2.7
Apple	4.2	5.3	4.5
Tabacco	9.4	10.3	9.9
Hevea	1.4	1.5	1.2
** Sea plant (SPM-1) (Ni: 18.6 ± 0.7)		19.5	17.9

* Standard reference material issued by the «Comité Inter-Instituts».

** Standard reference material from the International Atomic Energy Agency recommended value Ni: 18.6 ± 0.7 (standard error) mg/kg dry matter.

*** Determinations were kindly done by A. Wittenbach and P. A. Schubiger, Swiss Federal Institut for Nuclear Research, Würenlingen.

precision of the colorimetric and AAS methods

Samples	Extraction-ETA/AAS			Colorimetry		
	with background compensation					
	<i>N</i>	$\bar{x} \pm 1s$	<i>RSD</i> %	<i>N</i>	$\bar{x} \pm 1s$	<i>RSD</i> %
Grass	6	0.199 ± 0.009	4.6	8	0.195 ± 0.008	4.3
Barley corn	6	0.017 ± 0.002	12.9	8	0.018 ± 0.004	20.9
Barley straw	6	0.025 ± 0.002	6.9	8	0.029 ± 0.006	21.5
Winter wheat	6	0.035 ± 0.002	6.6	6	0.041 ± 0.004	8.5
Maize corn	5	0.036 ± 0.006	14.2	5	0.044 ± 0.007	17.1

\bar{x} = Ni content in mg/kg dry matter

Conclusions

The results obtained from the different methods are in good agreement. It can therefore be concluded that all the methods are accurate.

Thus, the choice of the method for routine analysis becomes dependent only on practical considerations. For the determination of nickel in sewage sludges, the flame-AAS was selected for its rapidity, in spite of its higher detection limit, whereas in the case of plant analysis only the electrothermal-AAS, preceded by extraction, comes out because of its higher sensitivity.

Methodological details

Ni-complex formation

Nickel reacts with dimethylglyoxime to give 2 different complexes, depending on the experimental conditions. Normally, the Ni(DMG)₂ complex is formed, but the Ni(DMG)₄ complex is obtained in the presence of an oxidizing agent.

At pH below 0.9 the dimethylglyoxime is not soluble, and a white precipitate is obtained. The addition of dimethylglyoxime in acid medium, above pH 1.1, is nevertheless crucial in order to avoid a precipitation of the nickel hydroxide.

Colorimetry

Extraction

Chloroform extracts Ni(DMG)₂, Cu(DMG)₂, dimethylglyoxime itself but not Ni(DMG)₄. In order to remove interferences from Cu, the organic phase

must be washed with dilute ammonia solution (1 : 200), as the Cu-dimethylglyoxime complex is soluble in alkaline solution.

Spectra and calibration curve

Due to its greater stability and higher sensitivity, the $\text{Ni}(\text{DMG})_4$ complex was selected for the colorimetric determination (fig. 1 and 2).

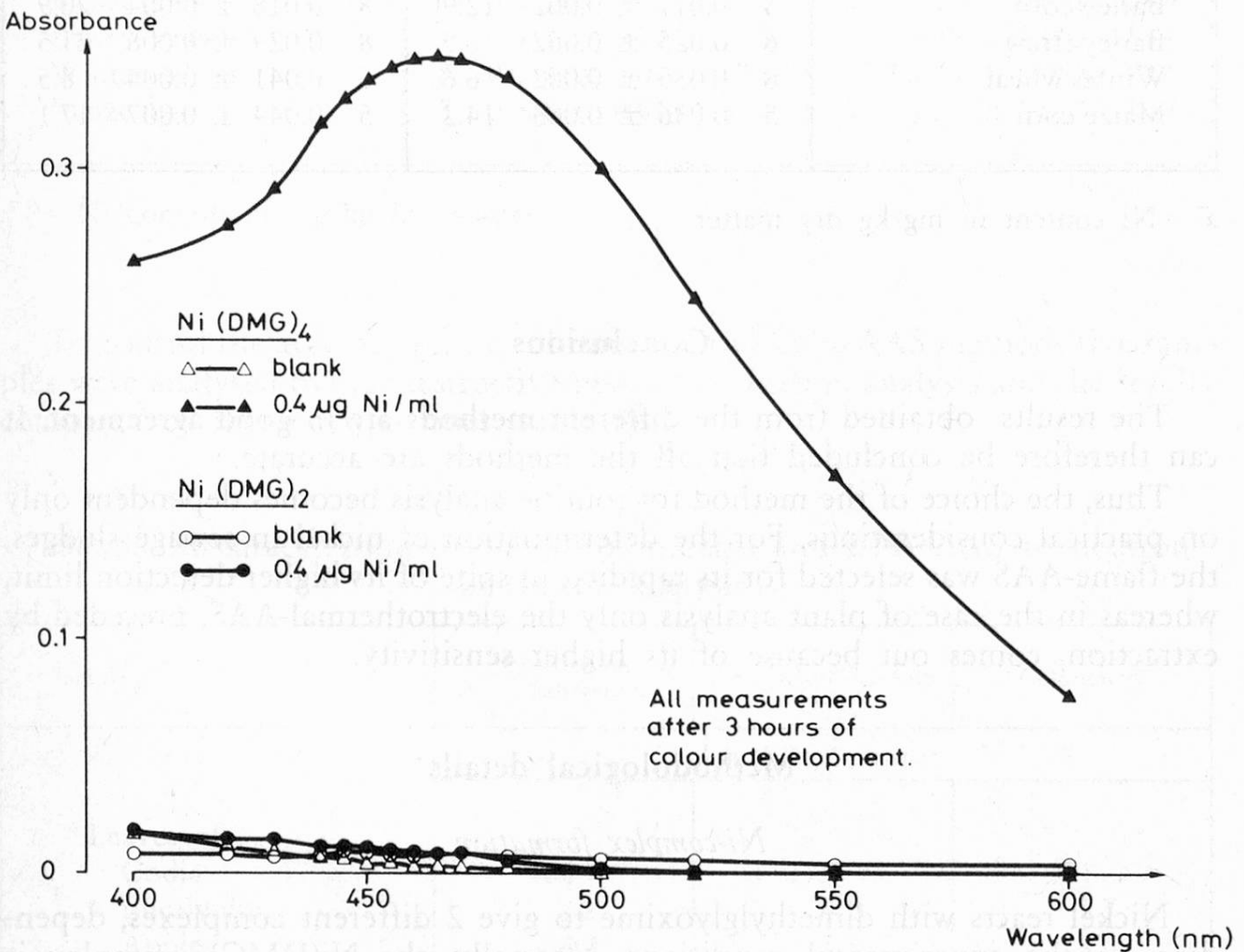


Fig. 1: Spectra of Ni-complexes

Interferences

Addition of the following cations to the nickel solution (10 μg Ni) showed no interference up to:

30 mg Fe (III)	as $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$
5 mg Mn (I)	$\text{MnSO}_4 \cdot \text{H}_2\text{O}$
3 mg Cu (II)	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
2 mg Co (II)	CoCl_2

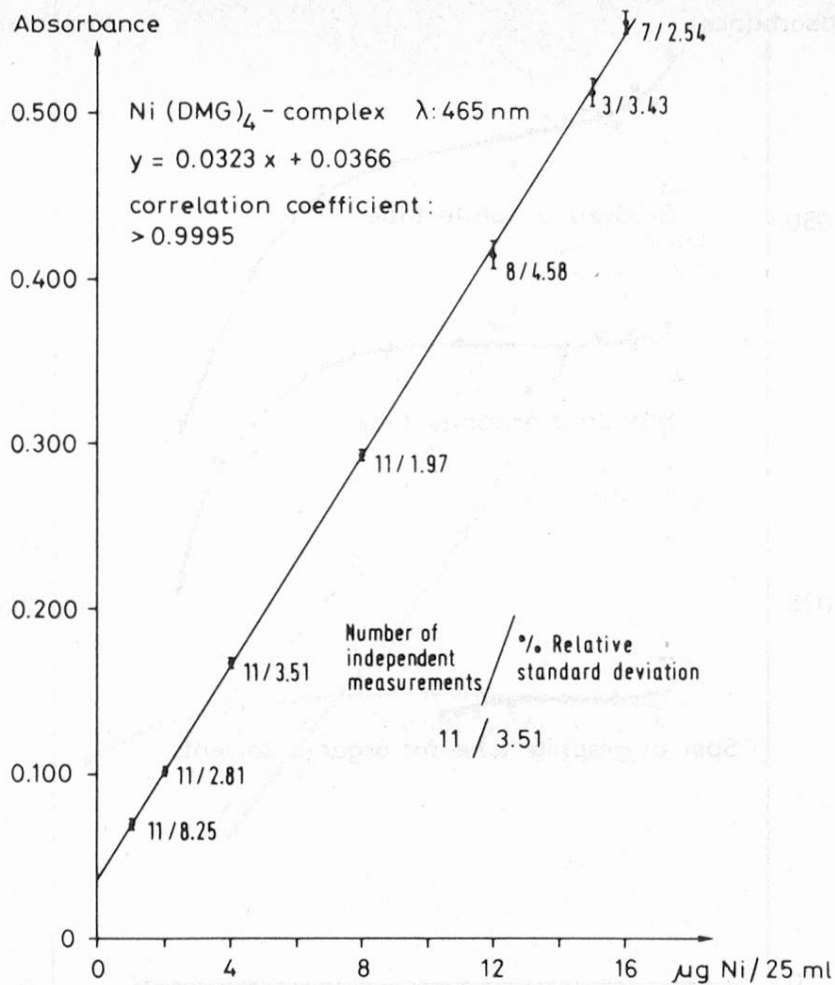


Fig. 2. Calibration curve

Extraction-Atomic absorption spectrometry

Choice of solvent

The required conditions were complete extraction and good burning properties. Solvents tested (in decreasing order of suitability): Xylene/MIBK*, Xylene, Xylene/DIPK**, MIBK, MIBK/DIPK, CHCl₃/MIBK. The Xylene/MIBK solvent mixture in the ratio of 70 : 30 was found to be the best one.

Extraction-Electrothermal atomization atomic absorption spectrometry

Conditions of measure

Three different graphite tubes can be used on the AAS-apparatus. They were tested under different mineralization and atomization temperatures, the results are shown in the figures 3 and 4.

Apparatus

Electrothermal-AAS	Perkin-Elmer 300 + HGA 72
Flame-AAS	Perkin-Elmer 420
Colorimetry	Metrohm E 1009 + Digital read-out device Optilab

* MIBK = methylisobutylketone

** DIPK = diisopropylketone

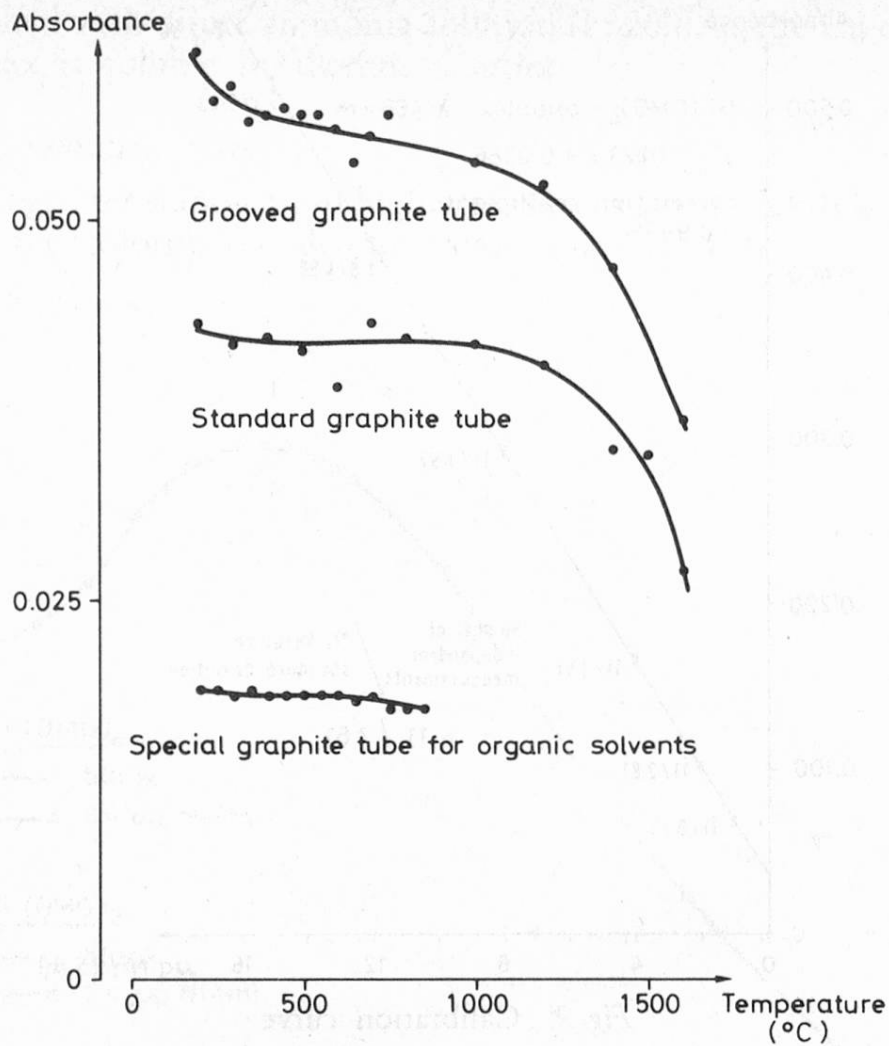


Fig. 3. Ni absorbance in function of calcination temperature

	Temperature °C	Time s
Drying	133	10
Calcination	variable	15
Atomization	2660	20
Injection	20 μ l = 1 ng Ni	

Acknowledgements

The analytical work was performed by Miss *M. Schuler*, the English translation by Mr. *J. Paul* and the script and diagrams were typed by Mrs. *I. Knecht*; to all we express our sincere thanks.

Summary

The determination of nickel in sewage sludges and plant material by atomic absorption spectrometry has been investigated in comparison to the colorimetric dimethylglyoxime

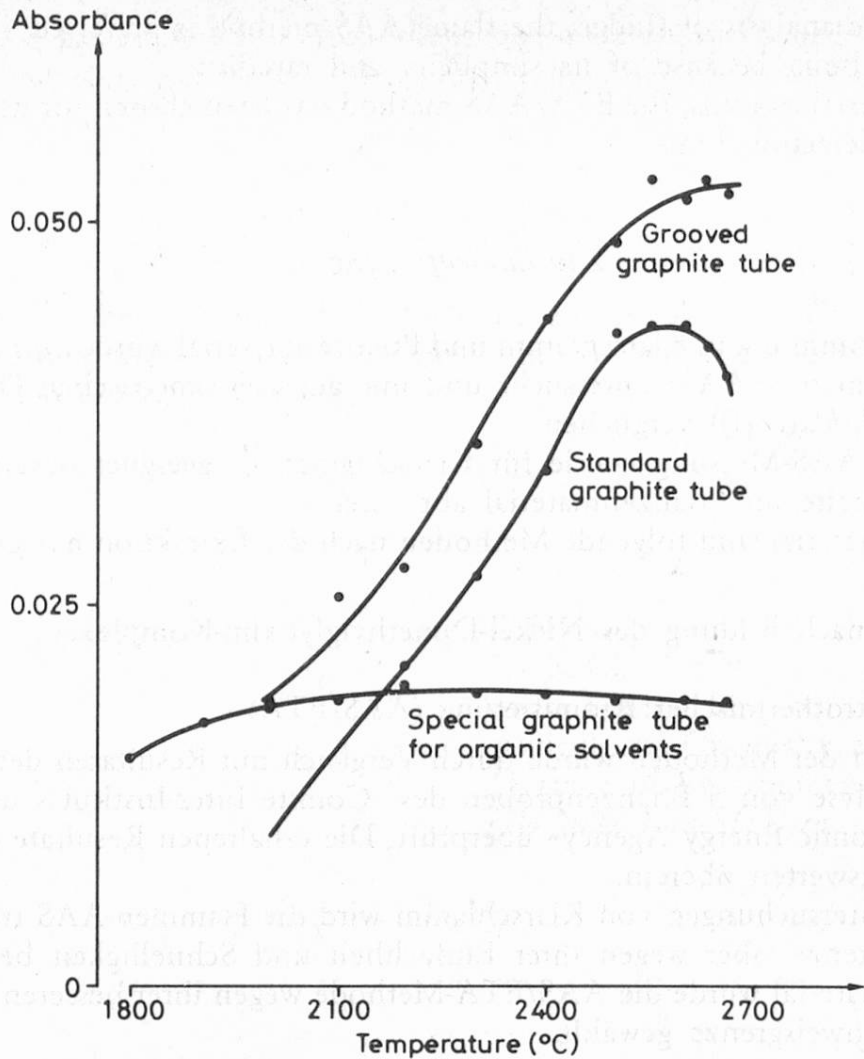


Fig. 4. Ni absorbance in function of atomization temperature

	Temperature °C	Time s
Drying	133	10
Calcination	600	15
Atomization	variable	20
Injection	20 μ l = ng Ni	

method (*Ölschläger* (1)). Flame atomic absorption measurement was proven suitable for sewage sludge, but unsuitable for the low contents in plant material.

For plant material, the following methods were suitable, after extraction of the nickel with dimethylglyoxime:

- Colorimetry, after formation of the $\text{Ni}(\text{DMG})_4$ complex
- Flame atomic absorption spectrometry (AAS)
- Atomic absorption spectrometry with electrothermal atomization (ETA/AAS)

The accuracy of the methods was tested by comparison with results of neutron activation analysis from 5 samples of the Comité Inter-Instituts and one from the International Atomic Energy Agency. The obtained results are in good agreement with the reference values.

For the routine analysis of sludge, the flame AAS method is preferred, in spite of its higher detection limit, because of its simplicity and rapidity.

For plant material analysis, the ETA/AAS method has been chosen for its better precision and lower detection limit.

Zusammenfassung

Die Nickelbestimmung in Klärschlamm und Pflanzenmaterial wurde mittels Atom-Absorptions-Spektrometrie (AAS) untersucht und mit der kolorimetrischen Dimethylglyoxim-Methode (*Ölschläger* (1)) verglichen.

Die Flammen-AAS-Messung wurde für Klärschlamm als geeignet befunden, für die kleinen Nickelgehalte im Pflanzenmaterial aber nicht.

Für Pflanzenmaterial sind folgende Methoden nach der Extraktion mit Dimethylglyoxim geeignet:

- a) Kolorimetrie: nach Bildung des Nickel-Dimethylglyoxim-Komplexes
- b) Flammen AAS
- c) AAS mit elektrothermischer Atomisierung (AAS/ETA)

Die Richtigkeit der Methoden wurde durch Vergleich mit Resultaten der Neutronen-Aktivierungs-Analyse von 5 Pflanzenproben des «Comité Inter-Instituts» und einer der «International Atomic Energy Agency» überprüft. Die erhaltenen Resultate stimmen gut mit diesen Bezugswerten überein.

Für Routineuntersuchungen von Klärschlamm wird die Flammen-AAS trotz ihrer höheren Nachweisgrenze, aber wegen ihrer Einfachheit und Schnelligkeit bevorzugt.

Für Pflanzenmaterial wurde die AAS/ETA-Methode wegen ihrer besseren Genauigkeit und tieferen Nachweisgrenze gewählt.

Résumé

La détermination par absorption atomique du nickel dans les boues d'épuration et les plantes a été comparée à la méthode colorimétrique à la diméthylglyoxime (*Ölschläger* (1)).

L'absorption atomique en flamme s'est avérée satisfaisante pour le dosage du nickel dans les boues d'épuration; elle ne l'est toutefois pas pour les faibles concentrations dans les plantes.

Pour celles-ci les méthodes suivantes ont été retenues, après extraction du nickel par la diméthylglyoxime:

- a) Spectrophotométrie, après formation du complexe $\text{Ni}(\text{DMG})_4$
- b) Spectrométrie d'absorption atomique en flamme (AAS)
- c) Spectrométrie d'absorption atomique avec atomisation électrothermique (ETA/AAS).

L'exactitude des méthodes a été vérifiée par comparaison des résultats avec ceux de l'analyse par activation de 5 échantillons de plantes du Comité Inter-Instituts et un de l'Agence internationale de l'énergie atomique. Les résultats obtenus correspondent bien avec les valeurs certifiées.

Pour l'analyse en série des boues, la méthode d'absorption atomique en flamme est préférée pour sa simplicité et sa rapidité, malgré sa limite de détection moins bonne.

La méthode par atomisation électrothermique a été choisie pour le matériel végétal à cause de sa meilleure précision et de sa limite de détection plus basse.

Literature

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