



Contaminated Soil Mapping (Heavy Metals). A Comparison of Atom Absorption Spectrometry (AAS) and X-ray Fluorescence Analysis (XRF).

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SUMMARY

Since the beginning of the eighties, the awareness of the problems regarding contaminated soils in the Federal Republic of Germany has been continuously expanding. As such contaminated areas may represent considerable danger, geological, hydrogeological, and chemical examinations of a suspicious area are unevitable. Sampling a large area containing a great variety of pollutants can therefore provide hundreds or even thousands of samples causing excessive costs for analyses.

In this publication, we want to demonstrate the compatibility of concentrations measured by XRF and AAS for the metals as mentioned in the German "Klärschlammverordnung" (Sewage Mud Regulation), and the "Leidraad bodensaneering" (Dutch List) [3].

Both XRF and AAS analysis provides comparable results. For the elements arsenic, lead, chromium, copper, nickel, and zinc, all the requirements of the Dutch List could be fulfilled. Exceptions were the elements mercury and cadmium. Detection limits of XRF analysis are within the B-values of the Dutch List.

Due to fast and inexpensive sample preparation and low costs per sample/element analysis, XRF analysis provide fast and inexpensive analysis of large sample quantities at high accuracy and reproducibility. This may allow, at same costs, a more narrow sampling pattern to ensure a more accurate localization of smaller anomalies and contaminated zones.

Anyway, the use of modern XRF analysis presents an environmentally safe analytical method which does not require disintegration of solid samples or waste management of acid solutions after measurement.

INTRODUCTION

Especially for the detection of heavy metals in contaminated soils it has been decided to look for a fast, reliable, and relatively inexpensive method of analysis. Well proven methods have so far been atomic absorption spectrometry (AAS) as well as atom emission spectrometry (AES). These methods, however, require the metals to be dissolved before being measured.

According to the official German Regulations of Water, Sewage, and Mud Unit Process, muds must be solubilized in nitrohydrochloric acid [1], which has also become useful for desintegration of soils.

X-ray fluorescence analysis (XRF) does not require this kind of treatment. Normally all elements from beryllium to uranium can directly be analysed in solids or pressed powder samples. Therefore XRF analysis is much faster than wet chemical methods providing at the same time a very high reproducibility of analytical results.

Reasons for the presently still existing prejudices regarding the use of XRF analysis in this kind of application are shown in the publication of MEDUNA & SCHÄFER [2] and are namely insufficient low limits of detection and a complicated handling for the traditionally trained chemical assistant.

An analysis method meeting the requirements of modern environmental protection, must therefore meet the following demands:

- For the individual elements, the detection limits must be so low that the values fixed in the "Leidrad Bodensanering" (Dutch List) [3] can be measured with high accuracy and reproducibility.
- Large sample quantities must be measured in a very short time in order to guarantee a dynamical coordination of laboratory and field work and a responsible risk management.
- Costs of analysis must be low, so that even a more narrow sampling pattern can be used for larger sample quantities enabling more accurate localization of smaller anomalies or contaminated zones.

In this publication, we want to demonstrate the compatibility of concentrations measured by XRF and AAS for the metals as mentioned in the German "Klärschlammverordnung" (Sewage Mud Regulation) [4]. The samples for this comparison are typical soils of a contaminated site. Table 1 shows the recommended values of the "Leidrad Bodensanering" (Dutch List) [3] and the German Sewage Mud Regulation.

Table 1: Recommended values of the "Dutch List" as well as the German "Klärschlammverordnung" (AbfKlärV/Novelle 91) in comparison to the detection limits of AAS and XRF in mg/kg (ppm).

	AbfKlärV		Dutch List			LLD	LLD
	Soils	Sewage Mud	A-Value	B-Value	C-Value	AAS	XRF
As	---	---	20	30	50	0.1	3
Pb	100	900	50	100	600	0.3	1
Cd	1,5	10	1	5	20	0.3	1
Cr	100	900	100	250	800	0.3	2
Cu	60	800	50	100	500	0.3	1
Ni	50	200	50	100	500	0.3	1
Hg	1	8	0.5	2	10	0.1	2
Zn	200	2500	200	500	3000	0.3	1

LLD = Lower Limit of Detection

A-Value = natural background (no contamination)

B-Value = requires further investigations

C-Value = requires sanitation

MATERIALS AND METHODS

Sampling and sample preparation

The sampling of the soil samples had been done by drilling. Each sample represents a sample of one drilled meter, and was homogenized and pulverized with a mortar in the laboratory. One part of the sample material was dried in a drying oven for two hours at a temperature of 105°C for determination of the solid content. The remaining material was dried at a temperature of 50°C overnight, in order to avoid losses of the very volatile metal compounds (esp. mercury). The dried samples were sieved (0.1 mm), then pulverized in a swing mill and simultaneously completely homogenized.

Atomic Absorption Spectrometry (AAS)

The AAS method requires the sample to be dissolved. The standardized procedure in this case is a dissolution in nitrohydrochloric acid (agua regia) [1]. 1.5 g soil powder is simmered for two hours with nitrohydrochloric acid (10.5 ml hydrochlorid acid, density 1.16 g/ml, and 3.5 ml nitric acid, density 1.40 g/ml; both are available from MERCK p.a.) in a fusion device including recycling.

Just above the recycling condenser, there is an adsorption device containing nitric acid in order to catch the very volatile compounds. The entire contents are quantitatively passed into a flask and filled with 0.5 normal nitric acid per 50 ml. Determination of the element concentration of the clear solution is carried out via a flame-AAS (Perkin-Elmer 2380) with a mixture of air and acetylene. The determination of arsenic and mercury is done by adding metal hydride and amalgam (Perkin-Elmer 3030). Sodium hydroboron is used as reducing agent in both cases. Element determination was carried out according to the current DIN 38405 and DIN 38406 [5,6]. Three standards has been used for calibration.

X-ray Fluorescence Analysis (XRF)

10 g of the soil powder mixed with 10 % spectral pure wax is pressed to a pellet of 4 cm in diameter at a constant pressing time and pressure. The pressed powder pellets are directly analysed. At this point, it is worth mentioning that XRF analysis is a non-destructive analysis.

XRF analysis is carried out with a modern sequential X-ray spectrometer with end-window X-ray tube (Siemens SRS 303) and the Siemens SPECTRA AT evaluation software using 41 international standards covering the complete range of all common rock and soil types. Matrix differences within the samples are automatically recognized and corrected by a specially developed and optimized evaluation program.

This enables a reliable analysis of samples with a widely varying composition of the matrix (major compounds) within one series. Total measuring time for the above mentioned 8 elements is less than 10 minutes per sample.

RESULTS AND DISCUSSION

The diagrams in Figure 1 to 4 show the results of analyses by way of comparison curves. The elements presented are chromium (Cr), copper (Cu), zinc (Zn), and lead (Pb). The parallels to the x-axis are the values given in the Dutch List for each individual element. The Y-axis is displayed in logarithmic division to show the excellent correlation even in the low-concentration range. Comparison curves for the remaining elements (Ni, Cd, Hg, As) are to be published later on.

The comparison shows that the analytical results of XRF correspond with the AAS values at a high accuracy in the required concentration ranges. All limiting values of the Dutch List can be determined, all existing anomalies were detected by both methods.

Analysing mercury and cadmium, there are some limits concerning XRF analysis. The Dutch List's limiting values (A-values) of mercury and cadmium in uncontaminated soils, are lower than the detection limits for XRF analysis of both elements. Therefore, analysis of very low concentrations of Hg and Cd within the range of the A- and B-values of the Dutch List, should be proved by AAS. But in most cases, concentrations of samples collected during a geochemical survey of a contaminated site may be within the range of the B- and C-values.

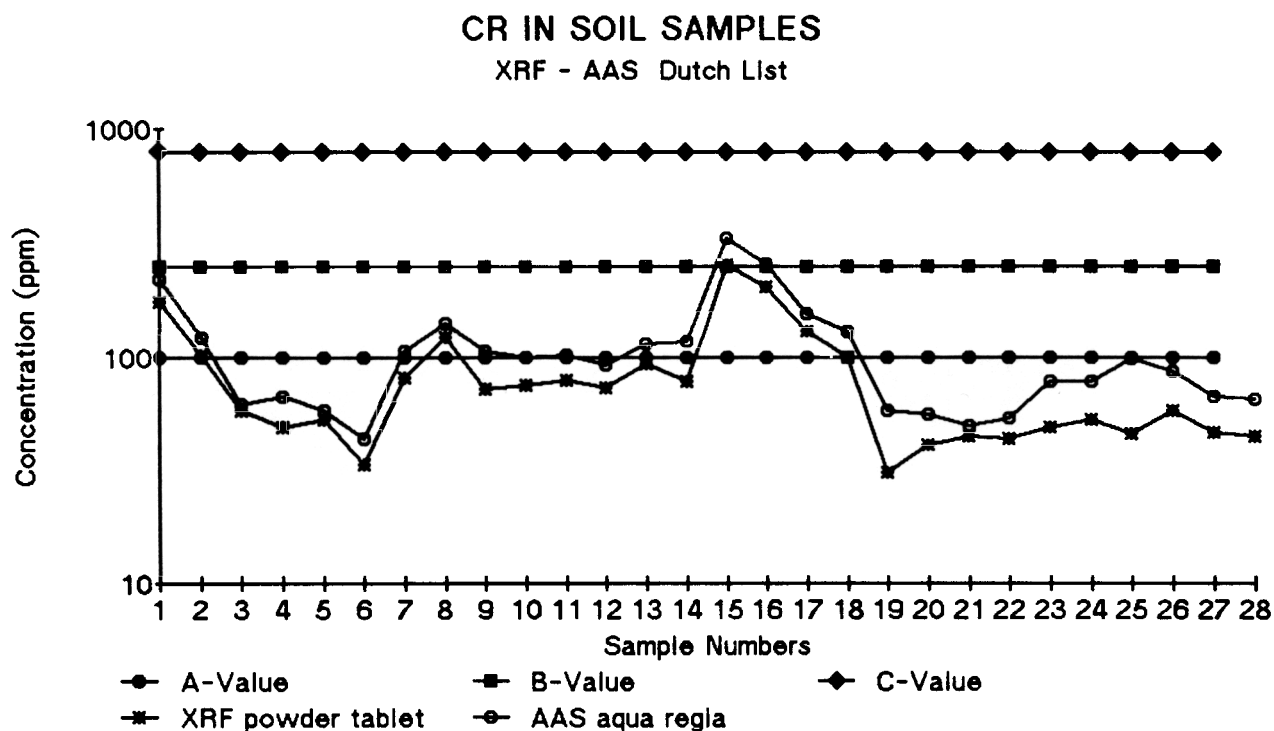


Figure 1: Comparison of AAS and XRF analysis of Cr in soil samples

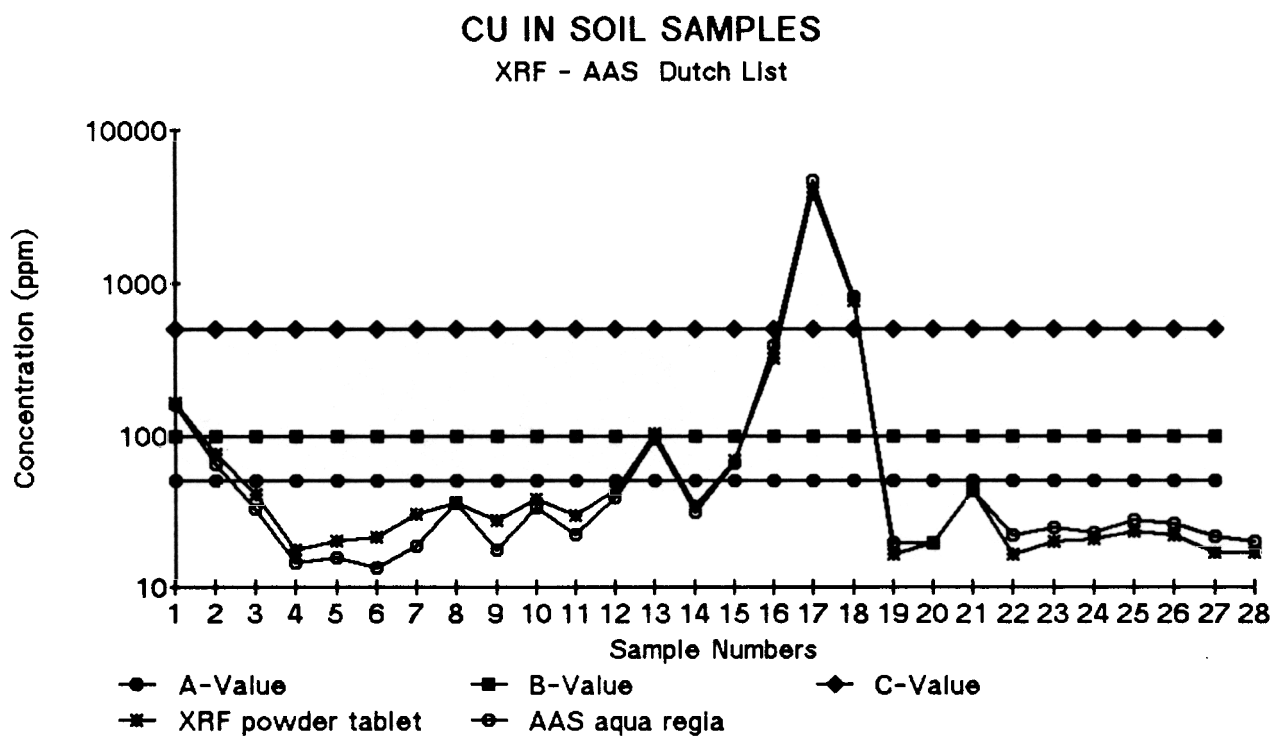


Figure 2: Comparison of AAS and XRF analysis of Cu in soil samples

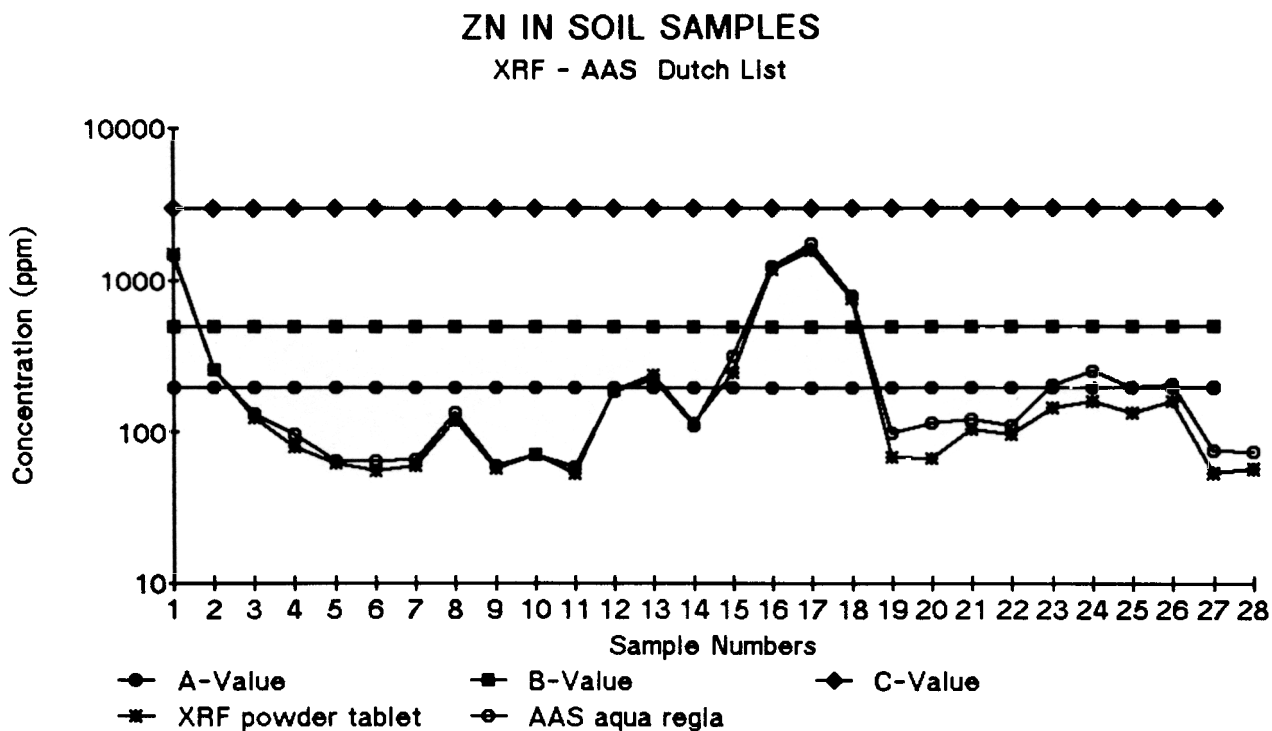


Figure 3: Comparison of AAS and XRF analysis of Zn in soil samples

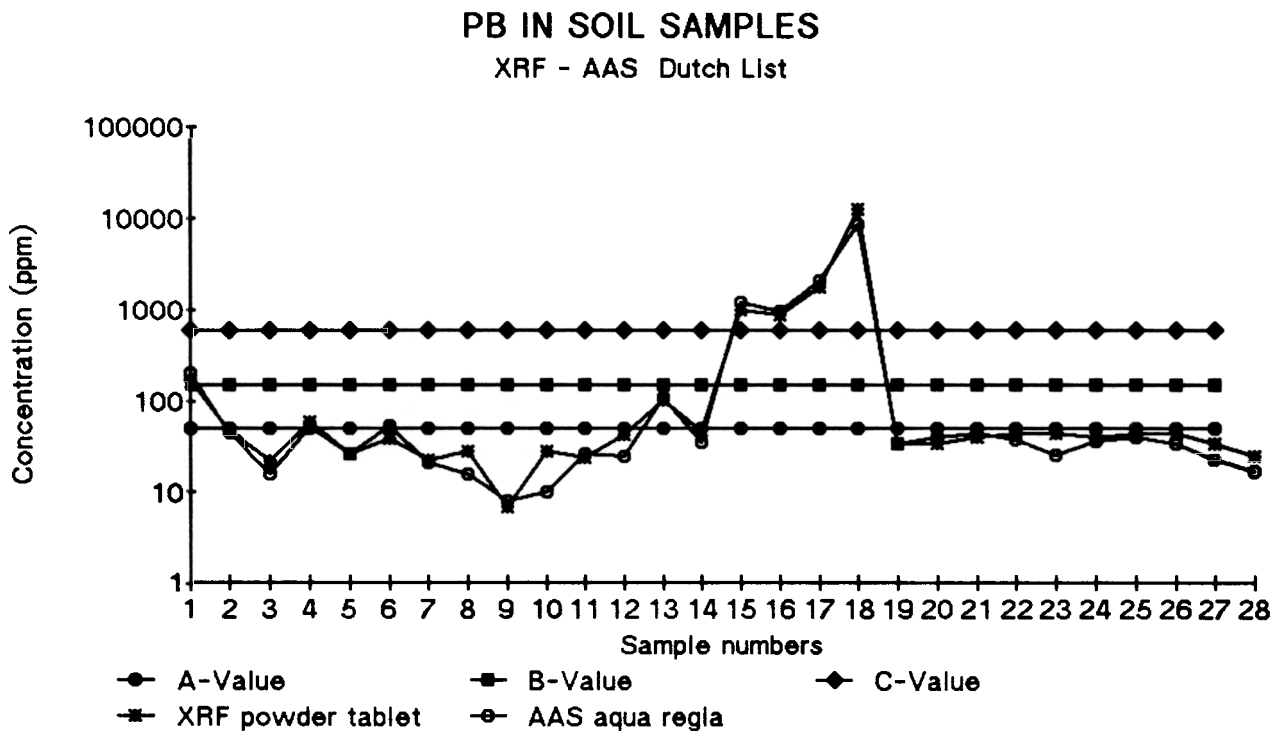


Figure 4: Comparison of AAS and XRF analysis of Pb in soil samples

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