



MODERNWATER

CASE STUDY

SENSPOL EVALUATION OF CADMIUM, LEAD AND COPPER ONSITE MONITORING OF WATER AND SOIL SAMPLES

The SENSPOL European Thematic Network aimed to enhance the development of sensors for practical applications in the abatement of water pollution.

Background

SENSPOL commenced in August 2000 and its role was to guide technological development of sensors for environmental pollutants. It accelerated the development of chemical sensors, biosensors and biomimetic systems to provide sensitive and robust devices for monitoring in water, contaminated soil and sediments.

Aim

The main objective of this evaluation was to compare the results obtained from the PDV6000 heavy metal analyser used under field conditions to the results from the same samples analysed in a conventional laboratory.

Samples from 5 locations in Germany were analysed. The target metals were Cadmium (Cd), Lead (Pb) and Copper (Cu). The samples were from various locations on the Rhine, and included a sediment holding area for dredged material, groundwater monitoring boreholes and 2 sites contaminated by former manufacturing gas plants. Soil and sediment samples were also analysed. A set of spiked samples from these locations were prepared to evaluate the effect of matrix and to indicate the analytical accuracy of the instrument.

PDV Setup

For analysis of Cd, Pb and Cu a mercury film carbon working electrode is required. The carbon electrode was first polished then a mercury film plated to the electrode surface. The PDV6000 was run using the VAS software so the instrument was connected to a laptop computer.

Sample Analysis

Water Samples

19 mL of unfiltered water sample, preserved with nitric acid at the time of sampling, was simply mixed with 1 mL of electrolyte. A single calibration standard was used for the analysis and quantification was by means of standard comparison.

A further QC check in the field is to spike a sample that has just been analysed with a known concentration of standard to check the recovery of the standard. If the recovery is less than 80%, the sample matrix is having an effect and the alternative method of quantification should be selected.



Significant matrix effects can be minimised by quantifying samples using the standard addition method. This procedure initially analyses the sample and obtains a peak if the target metal is present. A small volume of the target metal standard is then added to the sample and the solution is re-analysed. A second volume of the standard is then added and the solution analysed. The concentration in the sample is determined by using linear regression of the 3 peak heights obtained. By adding the standard into the sample matrix, most matrix effects on the mercury film are compensated for and a more accurate result is obtained. This method is only available when using the VAS software.

Sediment samples

Sediment from Tiefer See and Iffezheim were analysed. The Tiefer See sample was a black semi-liquid with a very strong odour of diesel and tar. This sample was field dried by pressing approximately 20g of wet sediment between sheets of filter paper. The dried material produced contained very fine particulate with approximately 30% moisture content. The Iffezheim sample was a light brown/yellow coloured material with no odour and low moisture content. This material was also made up of very fine particulate.

2g of each sediment were digested in 4 mL of concentrated nitric acid. To reduce the effects of organic compounds interfering with the analysis, 4 mL of hydrogen peroxide (30%) were also added to the mixture. In the presence of the organic compounds found in the Tiefer Zee samples, the reaction was exothermic causing vigorous foaming of the sample. The Iffezheim sample did not give an exothermic reaction. After the initial digestion 20 mL of electrolyte and 32 mL of pure water were added to the mixture to dilute the sample. The sample was left for 5 minutes to settle. 200 µL of this solution was added to 20 mL of electrolyte for analysis. Both samples were reanalysed using 2 mL of extract in 20 mL of electrolyte to detect Cd.

Results

Sample Location	Identifier	Sample Type	Pb (lab) ppb	Pb (PDV) ppb	Cd (lab) ppb	Cd (PDV) ppb	Cu (lab) ppb	Cu (PDV) ppb
I. Urmitz	spike	GW, P1	13	16.8, 11.4, 11.5 (recovery 108%)	12	14.8, 9.9, 11.5 (recovery 103%)	10	12.3, 12.2 (recovery 102%)
Iffezheim	spike	SW, P2	22	21.7, 21.8 (recovery 99%)	21	20, 19.7 (recovery 99%)	20	21.3 (recovery 106%)
Niederwerth	spike	NWP3	35	28.7, 30.5, 37.3, 29.1 (recovery 90%)	33	29.7, 35.5, 26, 33.2 (recovery 94%)	28	28.9, 22.2 (recovery 91%)
Kiel Canal	SI A	GW	25	25.5, 29.7	0.07	<5	9	<5
Kiel Canal	SI B	GW	21	21.9, 25.8	0.15	<5	7.1	6.8

Sample Location	Identifier	Sample Type	Pb (lab) ppb	Pb (PDV) ppb	Cd (lab) ppb	Cd (PDV) ppb	Cu (lab) ppb	Cu (PDV) ppb
Kiel Canal	Bl a A	GW	0.7	<1	<0,05	<5	1.8	<5
Kiel Canal	Bl a B	GW	0.6	<1	<0,05	<5	1.5	<5
Kiel Canal	Bl a C	GW	1	<1	0.06	<5	1.6	<5
Kiel Canal	S 2	GW	22	79, 100	0.28	<5	10	55, 51
Kiel Canal	S4 A	GW	4.7	4.4	<0,05	<5	0.9	<5
Kiel Canal	S4 B	GW	4.5	4.3	<0,05	<5	1.2	<5
Kiel Canal	S 9	GW	19	2000	0.24	<5	2	<5
Kiel Canal	S10 A	GW	4.3	4, 4.3	0.15	<5	1.5	<5
Kiel Canal	S10 B	GW	3.9	3.6, 4.3	0.09	<5	1.4	<5
Urmitz	I2	GW	0.5	<1	<0,05	<5	<1	<5
Niederwerth	I	GW	0.8	<1	<0,05	<5	<1	<5
Niederwerth	Irrig. well I	GW	1.4	1.1	0.13	<5	<1	<5
Tiefer See		SW	1.6	1	0.1	<5	2.2	<5
Tiefer See		IW	1.8	1.4	<0,05	<5	2.8	<5
Tiefer See		Whole Sediment		110 ppm		<1ppm (0.8ppm)		400ppm
Iffezheim		SW	1.2	1.5	<0,05	<5	<1	<5
Iffezheim		Whole Sediment		17 ppm		ND		12ppm

Laboratory method for metals: Pb, Cd, Cu (GF-AAS, DIN 38406-6, DIN EN ISO 5961, DIN 38406-7)

GW = Groundwater SW = Surface water IW = Interstitial water

Discussion

The results obtained for the spike samples showed very good agreement with what was expected for Pb, Cd and Cu. A recovery between 90 – 106% is within the acceptance limits of many laboratory analysers. The variation between replicate results was also acceptable for this type of instrument. The recovery of the spikes shows that matrix effects are unlikely to have affected the results from the sample analysis in this evaluation.

The results for Pb from the PDV6000 compared to the laboratory showed a very high amount of agreement except 2 samples, S2 and S9 from Kiel. These samples had a very strong organic odour. Sample S9 gave a very large peak in the Pb

window that was present on replicate analyses on different days. These large peaks were considerably outside the normal quantification range and are therefore only estimates of the concentration. The voltammogram generated for S2 after an x10 dilution showed a poorly defined peak with a peak centre at -350mV . A 20x dilution of S2 however gave a symmetrical peak with a maximum height at -450mV , indicating Pb was present in the sample.

It was interesting to note that the achieved MQL (minimum quantitation limit) for Pb in these samples was $1\ \mu\text{g/L}$, showing the high sensitivity of the instrument for this environmentally important toxic metal.

The results obtained for Cd using the PDV6000 also shows a good agreement, but only in respect of no false positive results. The concentration of Cd in all samples was significantly below the lowest estimated detection limit of 5 ppb. The spike samples do show that the PDV6000 can detect Cd at environmentally significant concentrations. One of the problems associated with early ASV devices was their susceptibility to contamination by organic compounds. Cd is very easily masked by organics, but the PDV6000 was able to detect this metal even in the spiked samples that also contained relatively high concentrations of organic compounds such as Poly Aromatic Hydrocarbons and BTEX.

The sediment from Tiefer Zee contained a very high concentration of organic compounds. The Cd result does show however that the PDV6000 was able to detect this metal even in this difficult matrix. The low concentration detected is consistent with the water results from the same area.

The results for Cu also show good agreement, but were surprising in the low levels detected. Sample Kiel S2 showed a 5x higher result than that obtained from the laboratory. This sample also showed an approximate 5x higher result for Pb. The sample results from the PDV6000 may therefore be due to more sample than required being added to the electrolyte. Alternatively a dilution error in the laboratory analysis could also account for these differences. The close agreement for sample Kiel S1B indicates a MQL of 5 ppb in this type of matrix. This shows the PDV6000 is sufficiently sensitive to accurately detect environmentally important concentrations of Copper.

Conclusion

The PDV6000 has been designed as a field based screening tool and not as an analytical instrument. A screening tool is a device that should provide analytical information that is relevant to the data requirement of the project. In most environmental projects, the analytical data requirement from a field instrument is to show if a sample is above or below a specified concentration of pollutant. An additional, but secondary, requirement is to indicate if the sample concentration is close to or significantly higher or lower than the specified concentration. The screening tool should also be useable by any field operator and be expected to reliably generate relevant data.

The results from this evaluation show that the PDV6000 can be used effectively in the field to identify if samples contain more or less than a user defined concentration of pollutant. The results for Cd, Pb and Cu show that the sensitivity, accuracy and precision of the PDV6000 method are also acceptable for quantitative data generation for environmental projects even under field conditions. The MQL for Pb and the estimated MQL for Cd are within the limits required for drinking water analysis.

The good agreement with the laboratory data for Cd, Pb and Cu, even when using a damaged working electrode shows the PDV6000 system to be robust for most metals.

