ON-SITE MEASUREMENT OF METALS IN WATER SAMPLES TAKEN FROM NANT GWYDYR AND LLYN GERIONYDD USING A COGENT ENVIRONMENTAL PDV6000PLUS METALS ANALYSER

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ABSTRACT

Heavy metals are the main cause of pollution from mine water but these are not routinely analysed and the main method of analysis is by spot sampling and then analysis at a laboratory remote from the sampling point.

This paper sets out to show how a well tried and trusted technology pioneered in the early 1980’s and now incorporating the latest electronic technology gives an easy to use method to measure heavy metals and provide information to enable mine operators to treat discharges in a cost effective manner.

It has been shown that the only reliable method of obtaining accurate results and mitigating damage to the environment is by on-line monitoring. We at Cogent environmental believe that real time analysis by on-line or portable heavy metal analysers is the best method of analysis, as real time results provide real time data and with real-time data real-time decisions can be made.

Relying upon results which may be several days old can be no real way to monitor or control a system.

It is generally thought that the metal content of mine water does not change appreciably but without real time continuous or semi continuous data how do they know the effect of rainfall events, variations in groundwater levels, collapses within the mine and localised seismic events .

We believe that new advances in Anodic Stripping Voltammetry technology provides a real opportunity for both researchers and treatment plant managers to monitor and deal with the problems associated with heavy metals in mine water.

1. DESCRIPTION OF ANODIC STRIPPING VOLTAMMETRY (ASV)

The method employs the ionic properties of metals. In this process the metal ions are first attracted towards the negatively charged working electrode where they are reduced to their metallic state onto the electrode surface being known as the deposition or plating phase during which the sample is stirred or agitated to prevent the formation of a depleted layer at the electrode surface.

Once this stage is complete the stirrer is stopped and the sample’s rotation is allowed to cease. The potential of the working electrode is then increased in the positive direction causing the metal which has been concentrated onto the surface of the working electrode to oxidise and the ions formed to flow back into solution in sequence. The flow of electrons caused by this oxidation reaction at the surface of the working electrode is measured by the counter electrode as a current and used to determine the concentration of the metal within the solution by the comparison of the cells response against a standard being run under identical conditions.

The graphs of voltage against current are known as voltamogramms and are used to identify the metal, quantification of the metal(s) is made by either comparison of either the peak area or peak height against a single standard of by multiple standard addition techniques which will give an indication of matrix interferences.

The materials used for the electrode, electrolyte used and the electrical conditions applied to the working electrode during the measurement cycle are all chosen to provide the best conditions for both selectivity and sensitivity for the given measurand.

Generally either Graphite Furnace Atomic Absorption (GFAA) or a version of Inductive Coupled Plasma (ICP) Spectroscopy is used to evaluate samples of water for metal concentration, however these analysis methods although perceived to be the ‘gold standard ‘ are not without their drawbacks. For example both ICP and GFAA are only able to deal with sample with less than 0.1%w/v dissolved solids[1] and there can be issues with As and Pb measurement.

2. NANT GWYDYR

History

Nant Gwydyr is a tributary of the Conway River and is classed by the Environment Agency of England and Wales as a polluted stream. Nant Gwydyr receives water from the adit of Par mine (mined sporadically between 1855 and 1963) and possibly Nant Uchaf [2]mine although this has not been proven. Under normal discharge conditions it is cited as contributing 1 tonne Zn, 0.2 tonnes Pb and 0.05 tonne Cd per year to the Conway[3]

Sample

A sample of the river water was taken from just upstream of a small bridge where a single track road passes over the river. Although the water was clear it was noted that there was an orange/brown deposit on the rocks in the bed of the river as can be seen in the photograph below.

Background

The evaluation of the sample was carried out on site at the side of the river in real time using the PDV6000plus and a laptop computer both operating on batteries.

As this was designed as a test of the ability of the PDV6000plus to analyse river water on site the expected concentrations of metals in the river were not made known to me and so the an estimate of the metal concentrations was made to set the initial scale. If the PDV6000plus was to be used for routine field applications the ‘normal’ ranges of metal concentration would be known and hence the volume of sample required.

Initially a 5ml sample of river water was pipette into the analysis cup of the PDV6000plus and when the sample was run a huge zinc peak was produced which was off-scale and swamped the peaks of the other metals present.

The next run was carried out using only 0.1ml of river water in 20ml of the electrolyte and the voltammogram from this run is shown below.:-

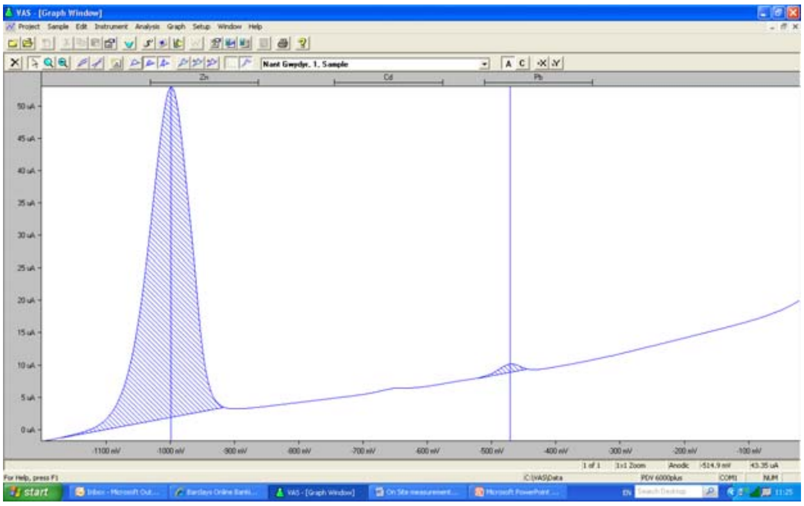


Figure 1. Voltammogram of sample from Nant Gwydyr

All ASV measurements are made by comparison against a standard or by standard addition to a sample. In this case the standard comparison method was used.

ASV results are linear over a measuring range of 10% - 200% of the standard value used in the comparison however; the results are at their most accurate when the peaks of the standard and sample are of similar height.

Figure 2 below shows superimposed standard and sample voltammograms, in this case a mixed standard of Zn, Cd and Pb was used.

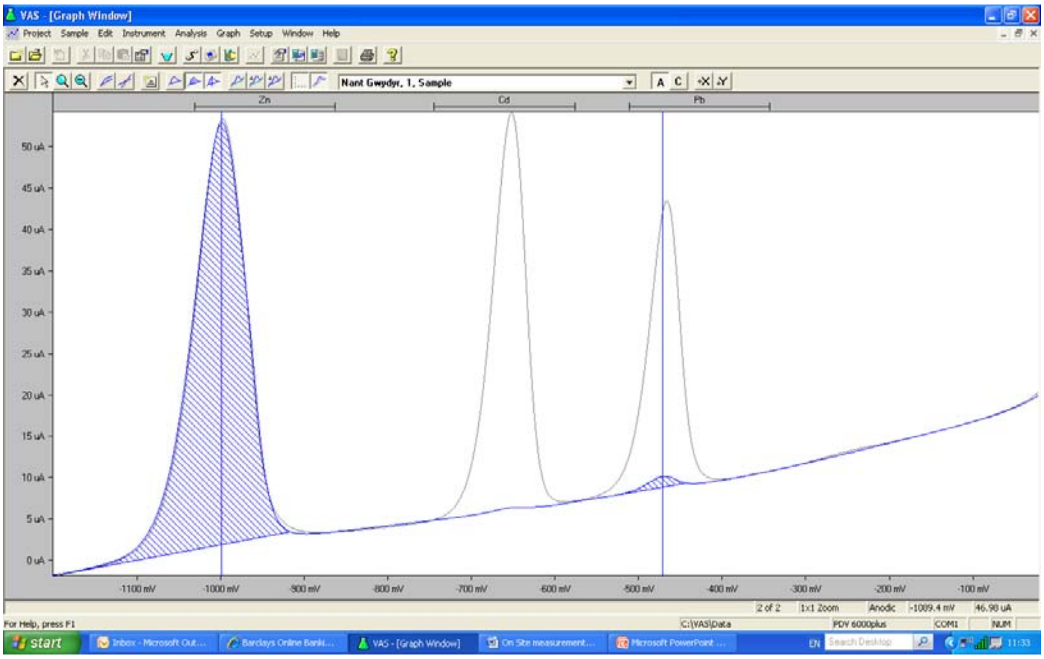
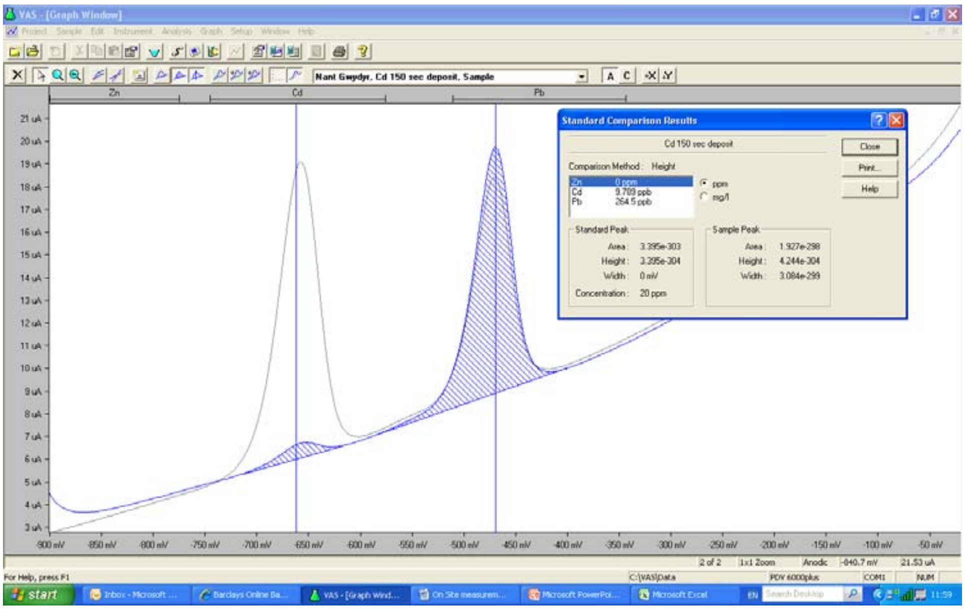


Figure 2

Here there is a clearly defined zinc peak (large blue hatched peak) from the sample scan which is almost exactly the same height as that of the standard (grey line). There is also visible a small cadmium peak and a slightly larger lead peak which require the ASV conditions to be changed to make them measurable as both of these peaks are less than 10% of that of the standard therefore outside the linear measuring range.

Re Run of Nant Gwydyr Sample to Improve CD and PB Resolution

The sample was then re-run using conditions which will enhance smaller peaks and compared to a standard of lower concentration the measurement window has also been adjusted to exclude the Zn peak to visually enhance the peaks of Cd and Pb the voltammogram is shown in Figure 3 below.



Cd 150 sec deposit

Comparison Method : Height

Zn	0 ppm
Cd	9.703 ppb
Pb	264.5 ppb

● ppm
○ mg/l

Standard Peak
Area : 3.395e-303
Height : 3.295e-304
Width : 0 mV
Concentration : 20 ppm

Sample Peak
Area : 1.927e-298
Height : 4.244e-304
Width : 3.084e-299

Figure 3

Results for Nant Gwydyr

From the data collected using the PDV6000plus the sample taken at from the Nant Gwydyr stream contains:

Zinc	2.08ppm
Cd	10ppb
Pb	265ppb

3. LLYN GEIRIONYDD

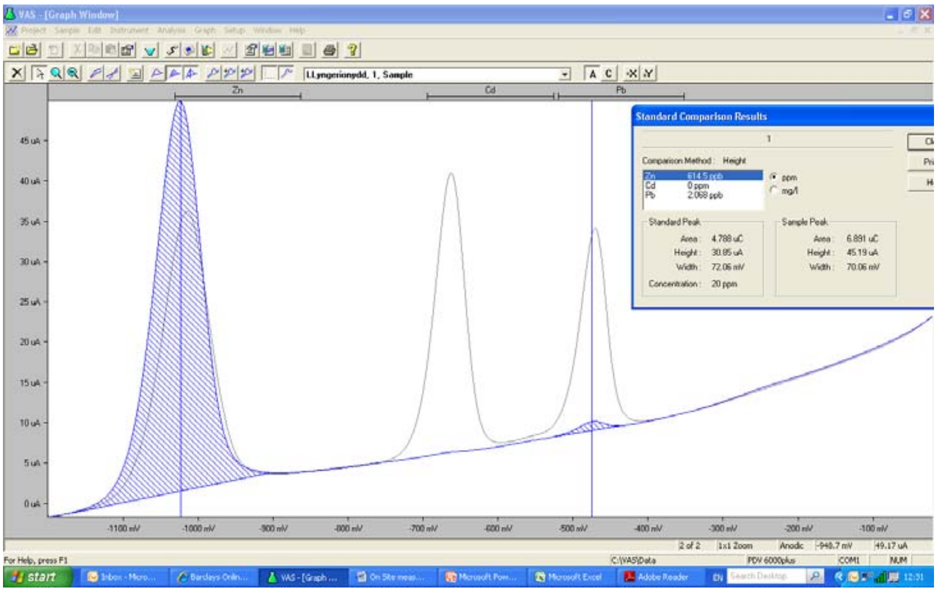
Background

The lake itself is just less than one mile long and is the only lake within the Snowdonia National Park where powerboats and water skiing is permitted. Part of the amenities of the lake (car park and toilets) are sited on the waste tip of the Pandora Mine. The exact source of the metal content of the lake measured at its outlet Afon Geirionydd is not known but is assumed to be from either the waste tips of Pandora Mine or from adit water. Local information suggests that there are little or no fish present in the lake which is assumed to be an artefact of the metal pollution.

Sampling Point

A sample was taken from the outlet of Llyn Geirionydd named Afon Geirionydd and analysed on site for the presence of Zn, Cd and Pb. The photograph below shows the exact sampling point with equipment used for the analysis.

Figure 4 below shows the voltammogram and results screen achieved from analysing a sample taken from the stream shown in the picture above which flows out of Llan Geirionydd.



Standard Comparison Results

1

Comparison Method : Height

Zn	614.5 ppb
Cd	0 ppm
Pb	2.068 ppb

● ppm
○ mg/l

Standard Peak

Area : 4.788 uC
Height : 30.85 uA
Width : 72.06 mV
Concentration : 20 ppm

Sample Peak

Area : 6.891 uC
Height : 45.19 uA
Width : 70.06 mV

Figure 4

To improve the sensitivity of the PDV to any cadmium and lead present in the sample the same procedure as used on the Nant Gwydyr sample would need to be employed, however it was decided that this was not necessary as the method had already been demonstrated.

Results for Llyn Geirionydd

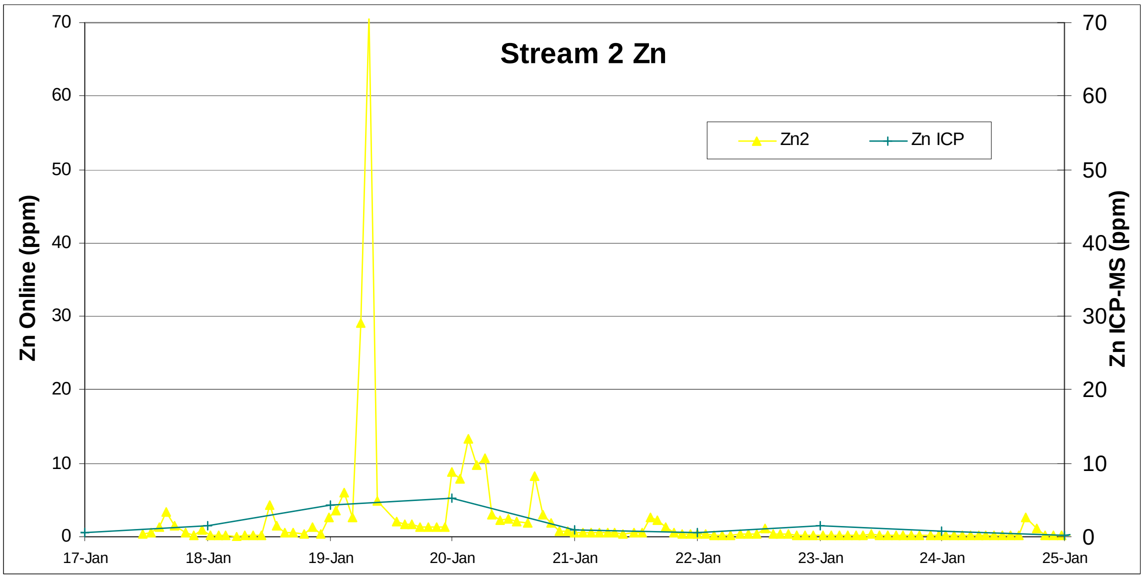
Zn	615ppb
Cd	not detectable under conditions used
Pb	1 ppb (enhanced conditions would provide better resolution of the Pb peak as in this voltammogram the sample's Pb peak is outside the linear range)

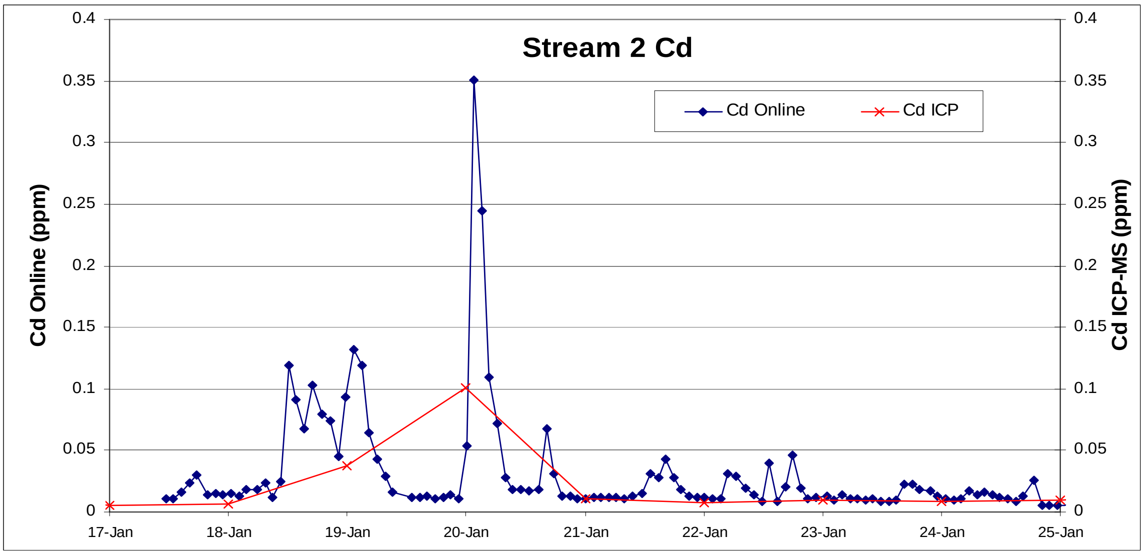
4. RESULTS

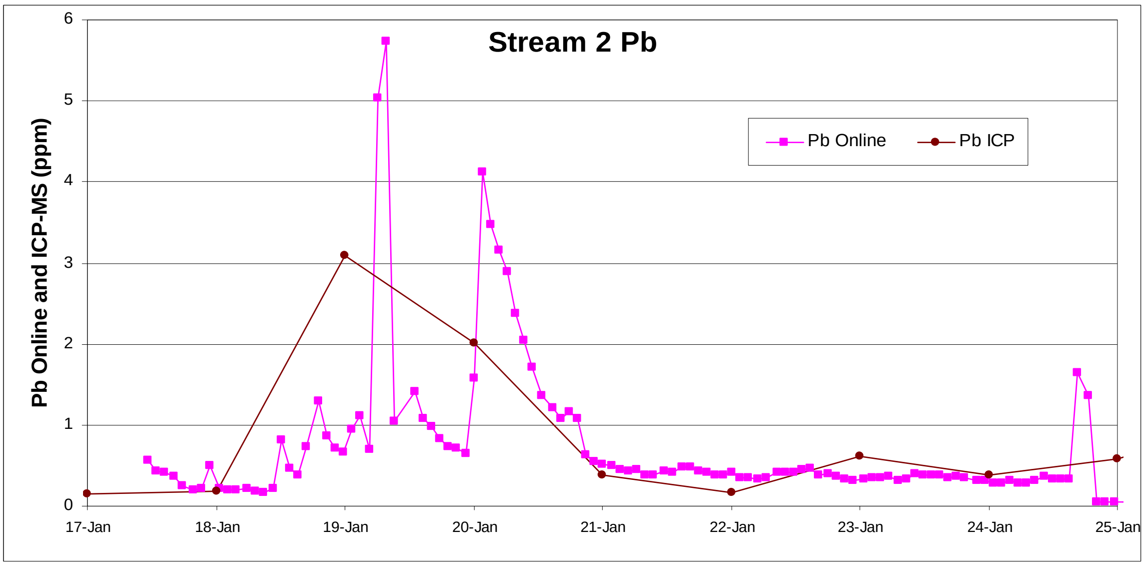
In both of the cases cited the approximate value was known by the Environment Agency staff as the values of metals were relatively stable over time therefore no samples were required for verification of the results.

The river water samples analysed in within this report posed no difficulty to the analysis method due to the lack of organics in the water sample.

Results from a more challenging sample are shown below these being from an on line anlayser monitoring effluent outfall from a smelter where the sample contained organics and other metals. In this case the results are compared against a 24 hour composite sample which was analysed using ICP







5. CONCLUSION

This report shows that the PDV6000plus is capable of measuring metals in real time at riverbank locations using minimal amounts of equipment the NiMH battery of the PDV6000plus providing a full day's operation of the instrument enabling several sites to be analysed in one day.

The results achieved here suggest that the concentration of zinc in the waters of both Nant Gwydyr and Llan Geirionydd both exceed the Environmental Quality Standards for fresh water[4] depending upon the alkalinity of the water which was not measured.

Acid Mine Water is an ideal analysis matrix for ASV due to the low concentration of organic compounds in the sample water and with the metals being in their labile forms requiring no sample preparation for evaluation. These labile forms of metals are also the most toxic to the environment being readily taken up by the flora and fauna.

Although no comparative data was available for the results achieved from the mine water analysis the analysis of a more difficult sample matrix from a smelting plant shows good correlation between the results from an online ASV analyser providing more detailed information on transients than is possible from discrete sample 24 hour composite samples as used in the case in question.

The aim of Cogent Environmental is to provide the means to determine heavy metals in real time allowing decisions to be made on current data and not historical values which are inevitable when having to send samples to central laboratories.

We believe that the results achieved from the visit to these two sites adequately demonstrate that Cogent Environmental's PDV6000plus provides useful data for the measurement of heavy metals on site. It can also be used to reduce laboratory costs by enabling the sampler only to send samples to the NLS which are close to or exceed the TLV for the particular measurand(s).

6. REFERENCES

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