



## Measuring trace metals on the spot

Want to know how much zinc and cadmium your local oysters contain, the level of mercury in a nearby watercourse, or the quantity of lead and arsenic in the neighbourhood soil?

Until recently you would have needed sophisticated measurement techniques only available in a laboratory. Now, thanks to collaboration between CSIRO and a Perth company, Chemtronics, a rugged reliable instrument is available for accurate trace-metal analysis in the field.

Called a portable digital voltammeter, the self-contained unit can, in a few minutes, measure levels of heavy metals in the 'parts per billion' range — that's like finding one piece of confetti on a tennis court. No wonder the instrument is proving its worth in environmental surveys and pollution monitoring.

Taking the instrument into the field has decided advantages over collecting samples and bringing them back to the lab. It avoids the problem of sample aging, and minimises contamination problems. Furthermore, the sampling pattern can be varied according to how consistently the results are showing up (for many years researchers have preferred on-the-spot measurements of pH, conductivity, and oxygen concentration, for this reason).

Because a microprocessor

controls its operation, the new instrument is easy to use. The operator only needs to press a few buttons on a keyboard. This factor and relatively low cost have meant that the portable digital voltammeter has become a tool of trade for increasing numbers of authorities and consultants.

The Western Australian Department of Transport has used one to check that lead levels in unleaded petrol dispensed from service stations complied with the statutory limit of 13 mg per L. Departmental officers were given operating instructions one day and began routine analyses at Perth service stations the next.

Other applications of the Chemtronics voltammeter have been to measure levels of:

- ▷ lead in blood and urine
- ▷ copper, lead, and cadmium leached from a mine tailings dump
- ▷ copper in tap-water (see the graph)
- ▷ cadmium in oysters (see the box)
- ▷ thallium and antimony in hot springs
- ▷ lead, copper, and bismuth in soil
- ▷ tin in canned food

In each case, the voltammeter measures tiny currents involved in a miniature electroplating operation. First, metals dissolved in the solution being sampled are concentrated by plating them onto a highly polished carbon electrode. For the best sensitivity, the electrode carries a thin mercury film in which the metals form an amalgam.

Then the voltage is reversed, and steadily increased; this strips the metals one by one, each metal coming off at its characteristic voltage. The size of the stripping current is directly related to the concentration of

the metal in the original sample.

The technique is both sensitive and robust. It is best suited to those metals that form amalgams with mercury — such as cadmium, lead, copper, zinc, thallium, tin, antimony, and bismuth — where levels down to 1 p.p.b. can be detected. For those that don't allow a mercury film to be used, like silver, gold, and, of course, mercury itself, detection levels some 50 times greater are typical.

The virtues of the technique — particularly the ruggedness of an electrode of mercury film on polished carbon, compared with other electrodes — were recognised 10 years ago by Dr Alan Mann and Mr Mel Lintern, of the CSIRO Division of Exploration Geoscience in Perth. Such an electrode, once

plated, will often last 100–200 analyses or several days.

But, to develop a portable unit, they saw that they must overcome two major limitations: the mercury-on-carbon electrode must not dry out between samples (otherwise its performance suffers); and the working electrolyte should both mop up any free oxygen and provide a universal medium compatible with most likely samples.

They found a unique electrolyte recipe that happily fulfilled the latter requirement. It calls for an alkaline solution of sodium chloride mixed with ascorbic acid (yes, vitamin C) as the antioxidant. The other requirement, for a permanently wet electrode, was trickier, but was finally



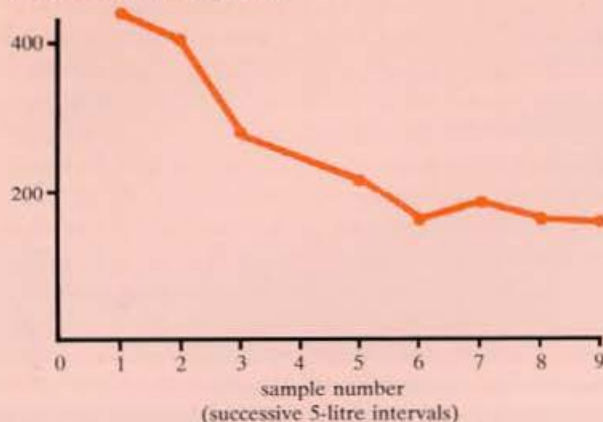
A portable trace-metal laboratory in the boot.



What's the level of heavy metals in this lake? Wait a minute and I'll tell you.

### Copper on tap

copper concentration (p.p.b.)



**If you brew your tea with water from the hot-water tap, you'll get an extra dose of copper from the copper pipes, as a portable digital voltammeter showed. (The tap had been off for 12 hours.)**

satisfied by a novel 'upside-down' sample cell. It's designed with electrodes inserted into a well at the bottom, so that some liquid always covers them.

It took them a few years' development and field testing (supported by the Australian Water Resources Council), but in the end Dr Mann and Mr Lintern ironed out the bugs and achieved their aim: a truly portable, accurate, and easy-to-use instrument for trace-metal measurement.

In 1985, Dr Mann decided to refine the instrument into a commercial unit, and he left his CSIRO job to form

Chemtronics and do so. The market's acceptance of the product of his labours has demonstrated the need for this valuable environmental tool.

Mr Lintern is continuing with research into voltammetry techniques; in particular, he is extending the list of elements that can be detected this way.

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Portable digital voltammeter for field analysis of trace metals. A.W. Mann and M.J. Lintern. *Australian Water Resources Council Technical Paper No. 83*, 1984.

## Cadmium in Shark Bay oysters

Big, beautiful, and isolated, Shark Bay lies 1000 km north of Perth on the Western Australian coast. Ringed by rugged red cliffs, its 8000 sq. km of shallow rich waters teem with dolphins, sharks, dugongs, crayfish, scallops — and oysters.

In 1982 a trial shipment of Shark Bay oysters was sent to Perth and, almost unbelievably, health authorities discovered they contained about twice the allowable concentration of cadmium of 2 p.p.m.

Where did the heavy metal come from? There's no big industry at Shark Bay, and no known mineral deposits, either. In 1984, the State Departments of Conservation and Environment and of Fisheries and Wildlife sponsored investigations into this puzzle, but the final solution awaited a subsequent study in 1986, funded by a Marine Science and Technology grant.

The work involved Dr David McConchie of the Department of Geology, University of Western Australia, and Dr Mann and Mr Lintern, of CSIRO, as

principal investigators. They took a prototype of the portable digital voltammeter to Shark Bay to gather clues.

Strangely, they found no cadmium in any of the fish; the only cadmium source they could find was a very low concentration (less than 1 p.p.b.) dissolved in sea water.

But in hundreds of on-the-spot analyses of oysters they found average readings of 4.5 p.p.m. One specimen contained a remarkable 49 p.p.m. of cadmium — many times higher than the maximum found near the lead smelter in Spencer Gulf.

Further probing provided a



**Dr McConchie and his assistant analyse Shark Bay oysters for trace metals.**

key, and Dr McConchie (now at the Northern Rivers College of Advanced Education in Lismore, N.S.W.) can now supply the answer: it's to do with the iron-rich cliffs that fringe much of Shark Bay.

When very fine iron-oxide particles wash into the Bay, they adsorb cadmium from the sea water to form an iron-cadmium complex. Measurements showed that cadmium levels shot up enormously whenever iron levels were elevated. Oysters are filter feeders, of course, and any suspended iron-cadmium complex eventually finds itself inside an oyster.

Here, the pH is lower and — *mirabile dictu* — the complex breaks down: the iron is expelled, but the cadmium remains in the animal. Hence, we have the world's only recorded case of oysters naturally rich in cadmium.

Heavy metals in marine biota, sediments and waters from the Shark Bay area, Western Australia. D.M. McConchie, A.W. Mann, M.J. Lintern, D. Longman, V. Talbot, A.J. Gabelish, and M.J. Gabelish. *Journal of Coastal Research*, 1988, 4, 51-72.