

A New Monitoring Method of Cr^{VI} in Water Using Boron-Doped Diamond Microelectrodes

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Boron doped diamond electrodes were used for the amperometric measurement of chromium^{VI} in water. A linear relationship of the current density as a function of the chromium^{VI} concentration was observed for concentrations comprised between 50 ppb and 4 ppm. Such results are particularly promising for the monitoring of chromium^{VI} in liquid effluents or process baths of several industries (stainless steel, electroplating, leather...).

Chromium^{VI} is an extremely toxic species with carcinogenic and genetic alteration effects on human beings. Typically, chromium salts are used in the manufacturing of stainless steel and alloys, in galvanic chroming processes, in cement manufacturing, in leather tanning as pigments, etc.^[1]. Effluents from such industries have to be controlled carefully so that their chromium content remains at an acceptable level regarding legal limits (below 100 ppb)^[1]. Moreover, in the future, allowed concentration level in effluents will certainly be reduced with the obligation to perform a continuous on-line monitoring. Currently effluent measurements are mostly performed manually as no "on-line" solution exists on the market yet. In this context it is interesting to perform on-line monitoring of hexavalent chromium concentrations with a maintenance-free and cost-effective electrochemical sensor.

Boron-doped diamond (BDD) microdisk-array-electrodes have already proven to be efficient for the detection of low concentrations of heavy-metals such as silver, copper, cadmium and lead^[2]. Results shown in the present report prove that they are also efficient in detecting toxic chromium^{VI}.

Electrochemical measurements were performed with a three-electrode system using a Ag/AgCl reference electrode and a platinum counter electrode. Microdisk-array-electrodes (MDA-5/150 with 537 microdisks) were used as working electrodes. Measurements were performed in 0.2M KNO₃ solutions by measuring the cathodic reduction of Cr^{VI}.

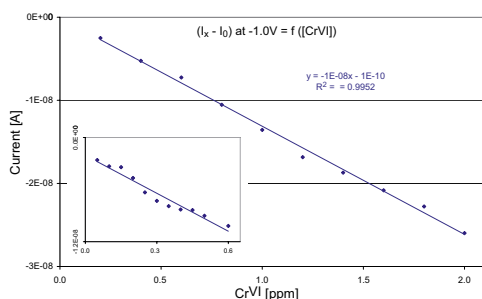


Figure 1: Evolution of the current measured at $-1.0V$ vs Ag/AgCl/KCl 3 M as a function of Cr^{VI} concentration in KNO₃ 0.2 M (MDA 5-150).

Figure 1 represents the evolution of the current as a function of concentration when measuring solutions of concentrations between 0.05 and 2 ppm of Cr^{VI} in 0.2 M KNO₃ with the microdisk-array-electrode. In such conditions, a limiting current for the reduction of Cr^{VI} of approx. -1.0 vs Ag/AgCl is observed. This figure shows that with such an electrode, Cr^{VI} concentrations in the ppb and ppm range can easily be measured, with the advantage that MDA electrodes allow measuring in media where conductivity is not well controlled.

For an accurate monitoring of steel industry effluents, measurement of Cr^{VI} should not be affected by other metal salts. One of the most abundant metal ions in stainless steel industry is Ni^{II}. Figure 2 shows voltamogrammes for solutions that contain various amounts of Ni^{II}. The inset chart shows the

current at -0.8 V as a function of the Cr^{VI} concentration for different amounts of Ni^{II}. This current is only correlated to the chromium content and totally independent from the nickel concentration. This is due to the fact that with BDD electrodes, Ni^{II} reduction occurs at approx. $+0.5$ V and thus does not interfere with the measurement at -0.8 V. Other potential interferences (i.e iron, zinc, lead) still have to be evaluated.

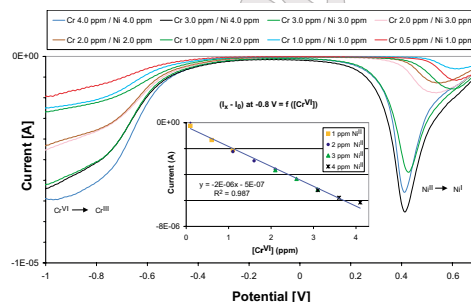


Figure 2: Evolutions of voltamogrammes and current at -0.8 V as function of Cr^{VI} and Ni^{II} concentrations.

These results show that BDD microdisk-array electrodes allow the measurement of chromium below the legal rejection level. Such BDD-MDA chips mounted in the three-electrode sensor BDD-SenSysTM and controlled with the electronic interface SenSys-ControlTM (figure 3) represent an ideal solution for the continuous monitoring of chromium containing effluents.



Figure 3: BDD-SenSysTM and SenSys-ControlTM.

The results presented here will be exploited for the development of such monitoring system in future projects.

We thank OFES for having supported this work.

[1] www.inchem.org/documents/ehc/ehc/ehc61.htm ; www.nature.nps.gov/hazardssafety/toxic/chrom_6.pdf ; www.epa.gov/IRIS/subst/0144.htm
 [2] C. Madore, A. Duret, W. Haenni, A. Perret, Proc. of the Symposium on Microfabricated Systems and MEMS V, P.J. Hesketh, H. Hughes and W.E. Bailey, Electrochemical Society Proc. Series, Pennington, US, 19 (2000) 159