



CHARLES UNIVERSITY IN PRAGUE
Faculty of Science
Department of Analytical Chemistry
ALBERTOV 2030, 128 40 PRAGUE 2, CZECH REPUBLIC

Prof. Ing. Karel Štulík, DrSc.
Tel: 00420 2 2195 1230
Tel/Fax: 00420 2 2491 3538
e-mail: stulik@natur.cuni.cz

A Review
of the PhD Thesis Entitled "Porous Electrodes for
(Bio)analytical Applications"
by Ing. Veronika Urbanová

This Thesis, prepared as the result of Ms. Urbanová's study jointly at the University of Pardubice and the L'Université Bordeaux 1, deals with a highly actual and important topic, namely, the preparation of sensors for trace analyses and for monitoring of signals produced by living tissues. The approach to this problem is also up-to-date and is based on the designing of porous electrodes based on bismuth and antimony and on modifying commercial microelectrode array sets with porous layers. The Thesis describes the preparation of the sensors, their operation and formulates some conclusions on their properties and their applicability. Actually, two rather different applications are joined together by the common principle of a porous electrode. Consequently, I have no objection in these respects.

The text of the Thesis has been prepared carefully and there are no formal problems. However, I have certain objections against the structure of the text. It flows freely, like a story, and it is difficult to find the point at which the description of the results of previous authors ends and the presentation of the present author's results begins – I set this point for myself at places, where references to the literature suddenly disappeared. It would have probably been better to follow the classical pattern: introduction - experimental - results and discussion - conclusions. The Thesis is based on the preparation of two porous electrodes and their application and this should have been the centre of the presentation.

It seems that the porous electrodes proposed should be useful in practice. The results presented in the Thesis support this and it would be useful to discuss it more closely. I would like to

point out some weaker points and suggest several topics for discussion:

- The data should have been generally statistically treated, considering some criteria more thoroughly, involving not only the detection limits but also, e.g., limits of quantitation, the linear dynamic range and some information on the accuracy of the measurements.
- What are the most important interferences - large-area electrodes generally suffer from adsorption of various substances, there will definitely be interferences from undesirable electrode reactions, etc.
- What are the lifetimes of the electrodes prepared?
- General applicability of these electrodes should perhaps be discussed more widely.

I recommend that this PhD Thesis be accepted for defence, discussed along these lines and then used as the basis for awarding the PhD degree to Ing. Veronika Urbanová.



Prof. Ing. Karel Štulík, DrSc.

Praha, 15. 3. 2010



Università
Ca' Foscari
Venezia

Dipartimento
di Chimica Fisica

Santa Marta
Dorsoduro, 2137
30123 Venezia

T +390412348535/8539
F +39 0412348594
dcf@unive.it
www.unive.it/dcf

Cod. Fisc. 80007720271
P.IVA/VAT
IT00816350276

Prof. Paolo Ugo

Dept. Physical Chemistry, Dorsoduro 2137, 30123 Venezia (Italy)

Phone :+39-041-2348503; e-mail: ugo@unive.it

Venice, April 2, 2010

Subject: PhD Thesis; candidate Veronika Urbanova

To Prof. Ivan Svancara

University of Pardubice

Head of the jury for the defense of PhD thesis

Branch P1419 Analytical Chemistry

The PhD thesis written by the candidate Veronika Urbanova presents the interesting results of a study aimed to explore the possible advantages coming from the use of microelectrodes whose active area has been enlarged by using template metal deposition to obtain macroporous surfaces. Two kind of application are explored. The first one concern with the generation of macroporous surfaces of bismuth and antimony to be exploited for the anodic stripping determination of cadmium and lead ions. The second application concern with the preparation and characterization of arrays of macroporous electrodes made of gold and platinum to be used in neurophysiological studies. The first application is typically an electroanalytical one, while the second moves the topics outside the usual frontiers of what is considered analytical chemistry, however the approach is typically "analytical".

In both cases, obtaining a large area electrode on a very small surface is crucial to improve the performances of the microelectrodes and the candidate engaged in a very difficult research work to explore such a possibility. The macroporous electrodes showed indeed improved performances in both applications, even if, perhaps, the improvements are not so dramatic as potentially expected.

The research performed required really a lot of careful experimental work since preparing the macroporous structures on the top of ultramicroelectrodes is not an easy task. Moreover, the experimental work is based on good fundamental knowledge presented clearly and with good depth in the introduction.

Overall, I can attribute a very positive evaluation. to the research work developed



by the candidate Veronika Urbanova and on the way it is presented in her thesis.

However, there are some points which require some correction to be inserted in the final version of the thesis, in order to keep everything in the right frame; they are listed below:

1. Chapter 3: it is not correct to define the bismuth film electrode as a sensor, as done in the title of the chapter as well as in the general conclusions section. This is because the bismuth film electrode does not possess any specific chemical recognition property; this is a property required by IUPAC in order to distinguish a sensor from a simple transducer or detector. The bismuth film electrode is simply an (advanced) electrode, as the antimony film electrode is or the Hg electrode was, but it is not a sensor.
2. Chapter 3, page 81. Detection limits are calculated as the concentration for which the signal to noise ratio $S/N = 3$. Please, explain how N is evaluated.
3. At the end of chapters 3 and 4 and in the general conclusion the candidate should honestly add some "things to be done" to complete the present study and to support the validity of the application of the macroporous electrodes for stripping analyses. In my opinion, they should include an evaluation of the possible memory effects (potentially very strong in a macroporous electrode) and a study on the possible formation of intermetallic compounds when performing analyses in real samples containing other metal ions in addition to Cd and Pb.
4. Page 88: ref.13 in the caption of Fig. 4-2 is indeed ref. 11
5. Table 5-1, Page 116: why the solutions of chloride salts or glucose, listed in the table, are mentioned as "buffer solutions"?

After these minor corrections, the thesis will be ready to be successfully defended by the candidate.

Prof. Paolo Ugo