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Microfabricated Chemical Analysis Systems for Environmental Applications

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Abstract. Recent contributions to the design, development, and fabrication of microtechnological devices for chemical analysis are summarized. The discussion includes microdisk-electrode arrays for voltammetric analysis of trace metals, and micro total-analysis systems for coulometric nanotitrations of different analytes.

Introduction

The development of microtechnological devices, including a wide range of sensors and actuators, is of primary interest and has a long tradition at the Institute of Microtechnology (IMT) Neuchâtel. In the past, several pioneering contributions were made, for example in the area of ion-selective field-effect transistors (ISFET) and related chemical sensors (for a review, see [1]). More recently, the research efforts were concentrated on design and fabrication of more sophisticated, complete microsystems. Such devices, as realized for chemical and biomedical applications, include sensor arrays [2], microreactors [3], and micro total-analysis systems [4].

Herein, we present an overview of some recent products of the research activities at the IMT.

Thin-Film Microelectrode Arrays for Trace-Metal Analysis

Miniaturization of electrochemical sensors has a considerable impact on electroanalytical chemistry, both in fundamental and applied areas. The advantages of microelectrodes, arising either from their small size or their special electrochemical properties, allow one to perform measurements which are inaccessible with conventionally-sized electrodes, as well as to implement new detection schemes.

One of the most active fields for miniaturized electrochemical sensors is the environmental analysis in general, and the stripping analysis of trace metals in particular. Application of voltammetric and potentiometric microsensors for on-site and *insitu* trace-metal monitoring would indeed allow to minimize errors associated with the collection and storage of individual samples for subsequent laboratory analysis.

The objective of the work performed at the IMT, in collaboration with the University of Geneva, is to realize voltammetric microsensors for trace-metal analysis in ground waters. These sensors are based on an array of 100 interconnected Ir microdisks and comprise also a containment ring for the controlled deposition of an antifouling membrane.

Such arrays were easily fabricated by thin-film technology [5][6]. Following the deposition of a bottom-passivation layer (LPCVD Si_3N_4) on the Si substrate, thin layers of the adhesion promoter Ta (200 Å) and of Ir (1200 Å) were deposited by

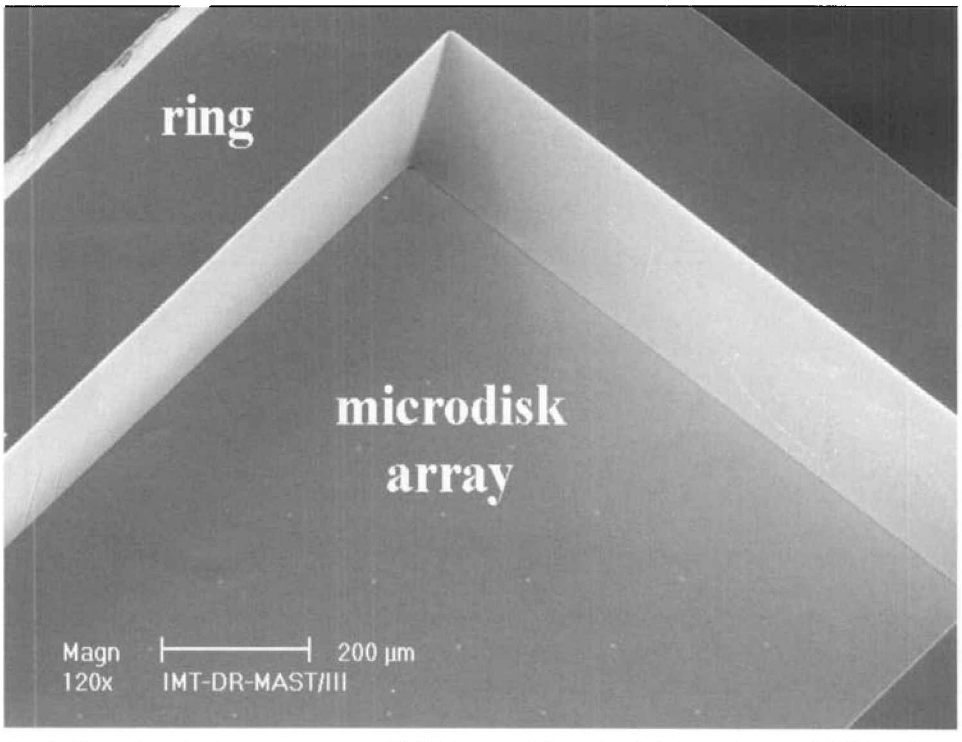

Fig. 1. *Scanning electron microscope* (SEM) *image of the microfabricated array of 100 Ir-microdisk electrodes, surrounded by a containment ring*

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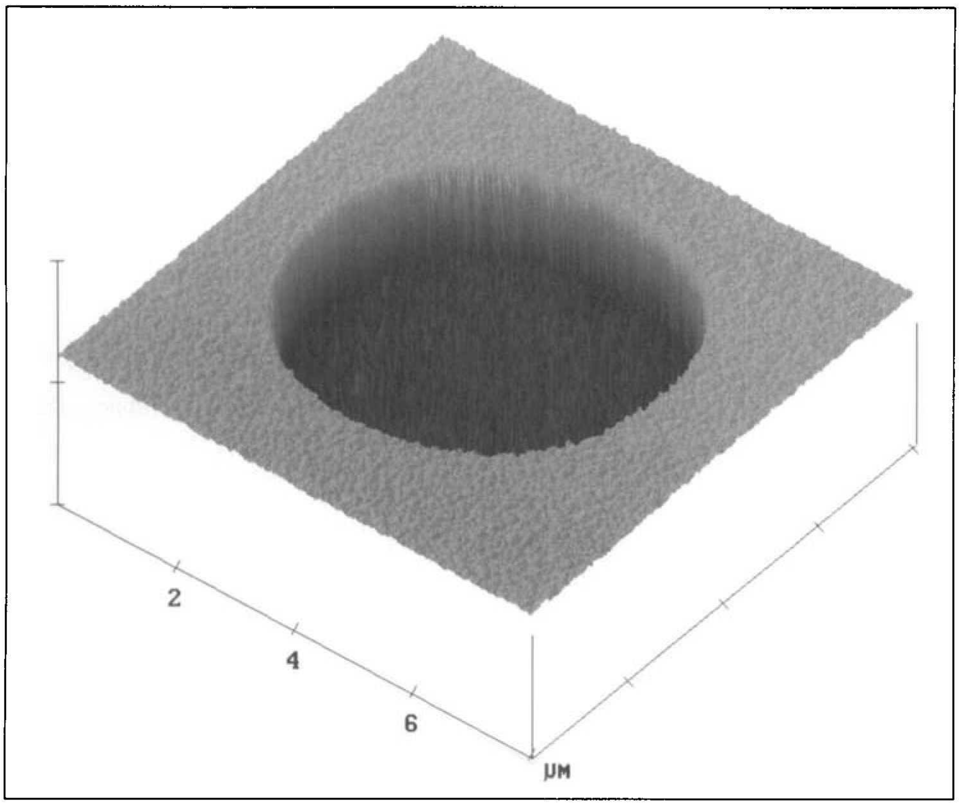

Fig. 2. *Atomic force microscope* (AFM) *image of a 5-µm diameter Ir thin-film microdisk electrode.* Measured electrode diameter: 5.4 µm; estimated electrode-surface roughness: 6 nm.

evaporation in a one-pump down process. A top-passivation layer was then formed (LPCVD Si_3N_4, 0.2 µm thick), and the microdisks and the connection pads were delineated by photolithography using a positive photoresist. The Si_3N_4 top-layer was etched in a SF_6/O_2 plasma. In the last step, a 300 µm thick *Epon SU 8* [7] containment ring was deposited and photolithographically patterned around the microelectrode array. The wafer was finally diced in individual chips, each containing an array of 5 × 20 microdisks of 5 µm diameter and 150 µm spacing, surrounded by the *Epon* ring (see *Fig. 1*). The full details of the fabrication procedures can be found elsewhere [5][6].

Before thin Hg films were deposited on the microelectrodes, the arrays were fully characterized using SEM and AFM studies and electrochemical experiments in ferrocyanide solution. These tests were carried out systematically in order to qualify the fabrication technology with respect to reproducibility and reliability. *Fig. 2* shows the AFM image of a single Ir microdisk located in an array. It can be noticed that the microdisk has an effective diameter of 5.4 µm, which well compares with the 5 µm initially designed, and a surface roughness of about 6 nm. Both parameters are uniform over the whole surface of the wafer. A reproducibility within ±2% was achieved for different batches.

Quasi-steady-state current responses of the microelectrode arrays were assessed by cyclic voltammetry in potassium hexacyanoferrate solution [6]. The excellent correlation between experimental and calculated values, as well as the absence of shielding effects, demonstrated the favorable specifications of the Ir microdisk-array sensors.

Analytical applications of the microelectrode arrays were worked out in collaboration with *Buffle* and coworkers (University of Geneva) [8]. The following procedure was developed for trace-metal analysis in environmental samples by square-wave anodic-stripping voltammetry. After a short cleaning period of 1 min at –0.1 V, metals are preconcentrated on the microdisk electrodes at –1.1 V for a given dep-

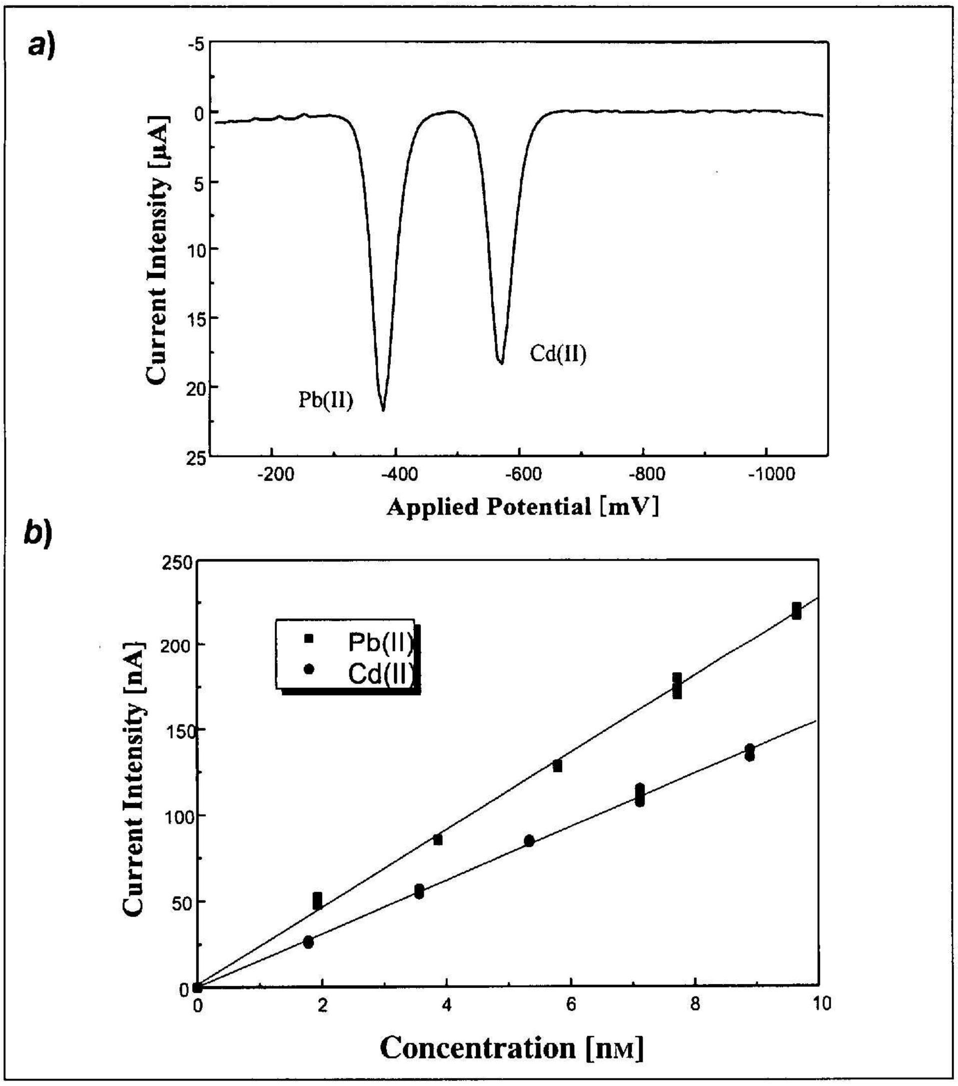

Fig. 3. *Square-wave anodic-stripping voltammogram* (a) *and calibration curves* (b) *obtained with an array of Hg-plated Ir microelectrodes in degassed 0.1M $NaNO_3$ solutions containing traces of Pb(II) and Cd(II).* Sample concentrations: *a*) 9.65 nM Pb(II) and 8.89 nM Cd(II); *b*) multiples of 1.93 nM Pb(II) and 1.778 nM Cd(II). Slopes in *b*): 22±4 nA/nM for Pb(II); 15±2 nA/nM for Cd(II). Auxiliary electrode: Pt rod; reference electrode: Ag/AgCl; current amplification in *a*): 100×.

osition time (typically 5 min for sample concentrations ranging from 1 to 10 nM). The potential is then gradually increased from –1.1 V to –0.1 V, using a pulse amplitude of 25 mV, a step amplitude of 8 mV, and a frequency of 50 Hz. From the recorded current values of the voltammogram, trace-metal concentrations can be determined with detection limits as low as 50 pM [8].

Fig. 3 shows preliminary results obtained from corresponding electroanalytical measurements. The experiments performed so far demonstrate the suitability of the microdisk-array sensors for *in situ* analysis of trace metals. At present, such Hg-plated and agarose-gel-integrated sensors are extensively used for both laboratory and field analysis of Pb^{II}, Cd^{II}, Mn^{II}, and Zn^{II} by square-wave anodic-stripping voltammetry [8].

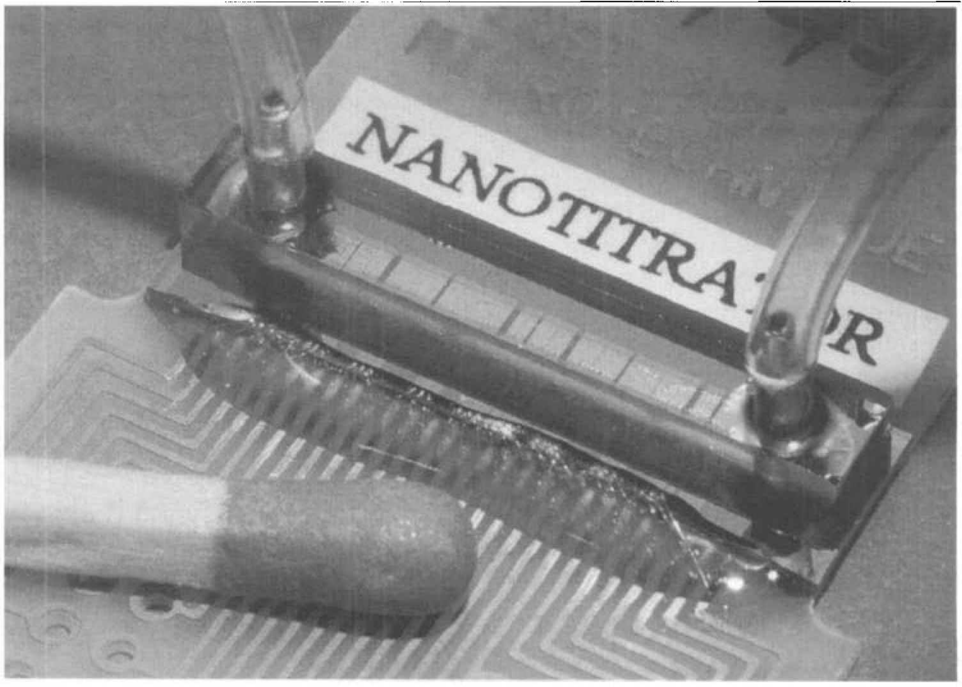

Fig. 4. *Photograph of the coulometric nanotitrator fabricated by microtechnology*

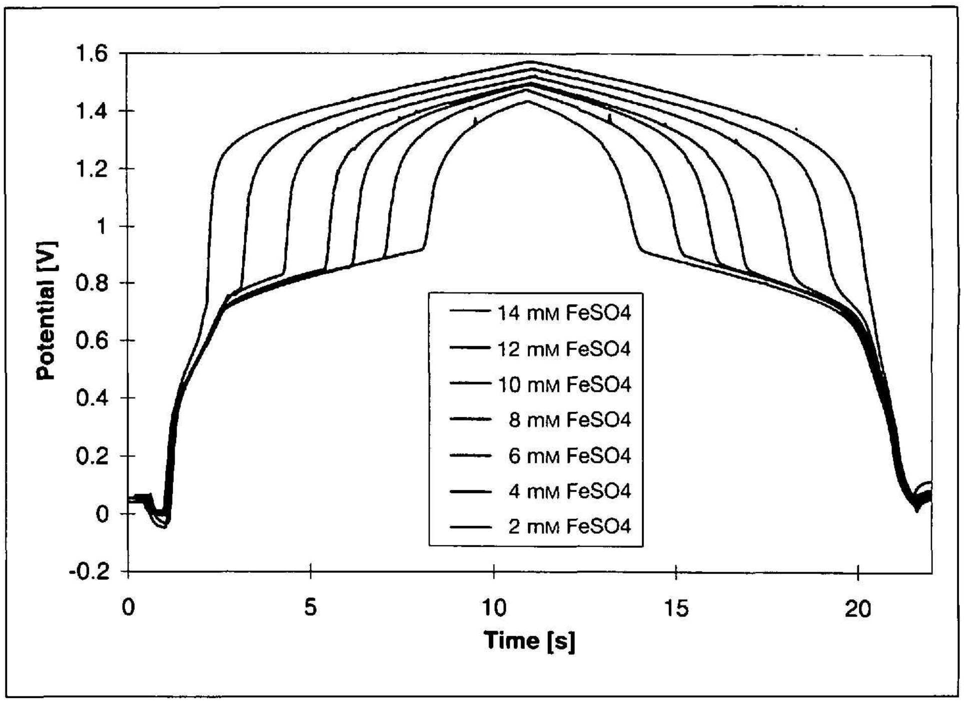

Fig. 5. *Typical response curves obtained for flow-injection coulometric titrations of Fe(II).* The sample concentrations ranged from 2 to 14 mM (curves from top to bottom). A triangle current-time profile with a slope of 8 μA/s was applied.

Microfabricated Analysis Systems for Nanotitrations

A prominent example of a micro total-analysis system developed at the IMT is the so-called nanotitrator, a titration system designed for the determination of nanomoles of analytes. Although titrimetric methods constitute a powerful group of quantitative procedures that find widespread use in analytical chemistry, their application was so far restricted to macroscopic samples. A real large-scale miniaturization of titrators was achieved only recently, when flow-through devices with coulometric electrodes for the generation of titration reagents and potentiometric electrodes for endpoint detection were realized [9][10].

The nanotitrator shown in *Fig. 4* was fabricated by well-established procedures of silicon/glass chip technology [10]. It was made of two parts, bound together by anodic bonding: a silicon substrate on which planar Pt electrodes were deposited, and a glass cover in which a channel was etched. First, a thermal oxide was grown on the Si substrate and then partially etched in buffered HF. By this procedure, a 1600-Å thin cavity was created, into which the Ta-supported Pt-electrode layer was deposited. The nonmetallic surface of the substrate was then covered by a Si_3N_4 insulation layer. The microchannel in the *Pyrex* glass cover was etched with 50% HF. A LPCVD polysilicon mask, defined by plasma etching, was used to protect the glass surface. The inlet and the outlet of the channel were made of two holes, ultrasonically drilled. Before the bonding step, the polysilicon mask was removed in a KOH bath. Anodic bonding of the glass surface with the nitride layer of the support was completed at 450° by applying a voltage of 1.2 kV. In devices used for argentometric titrations, the Pt electrodes were finally coated electrochemically with an Ag layer. Further details on the complete fabrication procedures may be found elsewhere [10].

The nanotitrators were successfully applied for argentometric titrations of chloride and thiosulfate, for redox titrations of Fe^{II}, as well as for acid-base titrations [9] [10]. Excellent specifications were achieved for quasi-steady-state titrations that were performed under stopped-flow conditions. In these experiments, the titrating reagent was generated at a constant rate by switching on a given current at the coulometric electrodes. The titration of the analyte proceeded in an effective sample volume of about 200 nl and was detected by the potentiometric indicator electrode. In all applications studied so far, it was possible to detect nanomoles of analytes in submicroliter samples with a precision of ±1% after a total analysis time of only a few seconds [9][10].

Using the same devices, continuous-flow coulometric titrations can be carried out as well [11]. To this end, a triangle current-time profile has to be applied at the coulometric generator electrodes, as described by *Pungor et al.* for macroscopic analysis systems [12]. The first period (leading edge) of such a triangle input signal generates increasing amounts of the titration reagent, whereas the second period (trailing edge) results in the injection of decreasing amounts of titrant into the flowing sample. Evidently, corresponding titrations can be performed and recorded in both directions, that is, for increasing and decreasing amounts of added reagent. *Fig. 5* shows a set of response curves that were obtained for flow-injection redox titrations of samples with different Fe^{II} concentrations. As expected, two equivalence points are found for each titration curve, namely, one on the leading edge and the other on the trailing edge of the curve. The time interval between the two points is obviously related to the actual sample concentration.

Very recently, an even more sophisticated microsystem was developed which may be suited for both coulometric and volumetric titrations [4b]. This micro total-analysis system (μTAS) integrates a flow-through channel with an electroosmotically driven nanopump, and an actuator/sensor cell for coulometric titrations with potentiometric detection (see *Fig. 6*). The complete device was microfabricated from a glass substrate. One outstanding feature of the electroosmotic dosage system is its ability to pump solutions with typical flow rates in the range of only some nanoliters per minute. Work aiming at a full characterization of the new device is in progress.

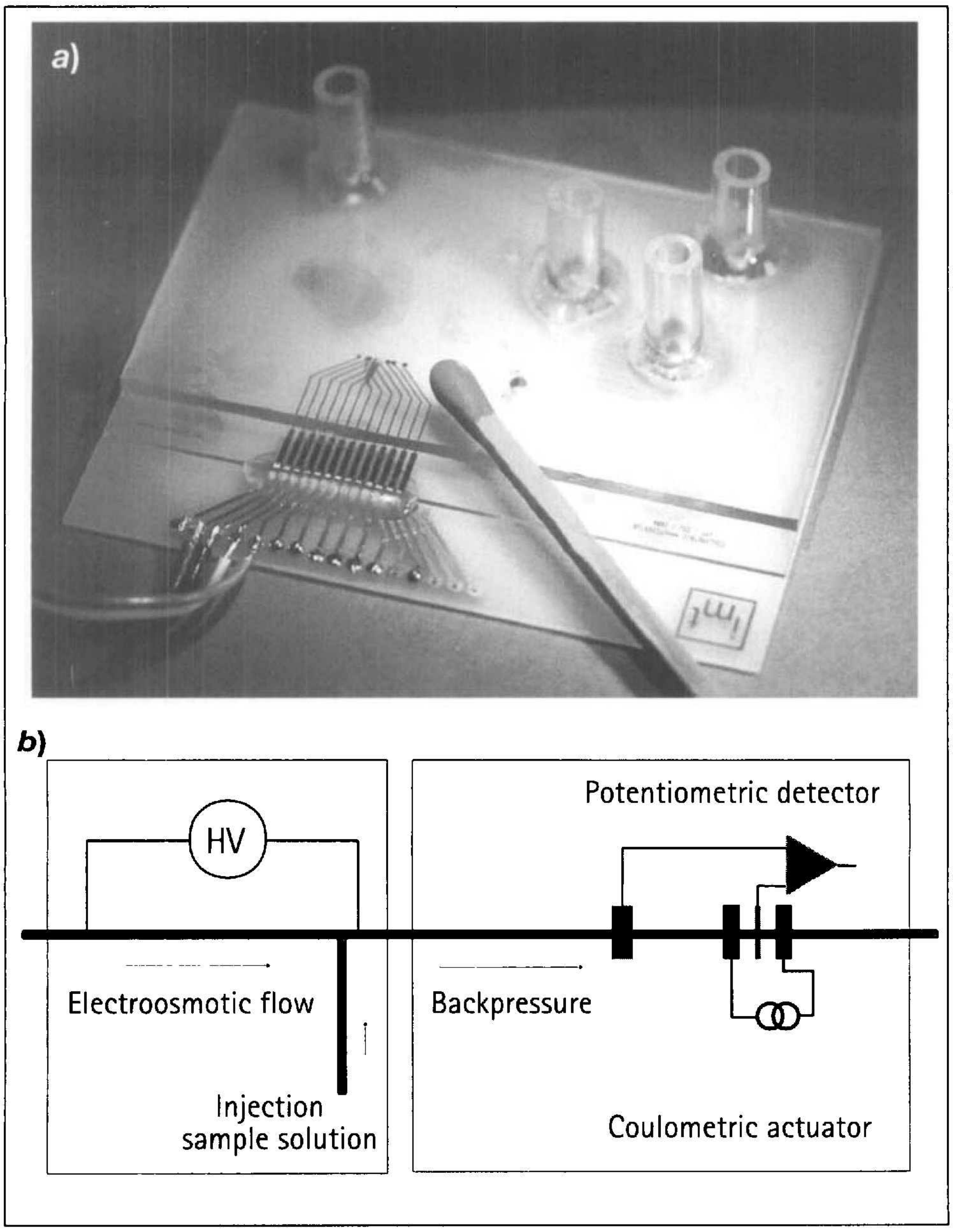

Fig. 6. *Photograph* (a) *and schematic view* (b) *of the micro total-analysis system (μTAS) for coulometric nanotitrations.* In *a*) the sensor and actuator-electrode array is located at the left of the match, and the electroosmotic pump in the upper part.

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