IMPROVEMENTS IN AUTOMATIC ELECTROCHEMICAL ANALYSES, USING THE PAR 374

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INHOUD

SUMMARY

The electrochemical analysis system PAR 374 has been improved by several modifications, involving automated standard additions directly into the sample cell, a modification of the paper advance control, the construction and incorporation of a rotating disc (Glassy Carbon) Electrode and a drastic decrease in the consumption of nitrogen. The addition of a pH-stat -using CO_2 gas- ensures a constant pH during the measurement, with minimal contamination problems.

SAMENVATTING

Verbeteringen aan het electrochemisch analyse systeem PAR 374 worden beschreven. De standaard addities geschieden nu direct in de cel; hieraan gekoppeld is het papier transport veranderd. De conctructie en inbouw van een roterende Glassy Carbon schijf-

electrode (GCE) wordt beschreven. Het gebruik van stikstof wordt drastisch beperkt. Toevoeging van een pH-stat, gebruik makend van CO_2 gas, maakt het mogelijk de pH constant te houden gedurende de analyse, met minimale kans op contaminatie. Bij de veranderingen is uitgegaan van de mogelijkheid om alles makkelijk in de oorspronkelijke staat terug te brengen.

I. INTRODUCTION

Electrochemical techniques find an increasing number of applications all over the world, in particular in the field of environmental analysis. The advantages are the possibility of multi-element analyses at very low concentration levels without the need for chemical pretreatment of the sample (thus limiting contamination problems) with a small, relatively cheap instrument. The techniques involved are not simple however. They require - like most analytical techniques - skilled people, being able to recognize the occurrence of malfunctioning equipment. One of the disadvantages of the electrochemical techniques is the relatively long analysis time. An analysis of heavy metals in marine samples takes normally more than one hour. Automation of the analysis seems to be one of the answers to this problem. The only polarographic analyzer with the possibility of automated operation is the PAR 374 combination (E.G. & G.).

Basically the 374 has been working well. However we have found artefacts in the operation of the machine which were either basically incorrect or unpractical in use.

The standard addition procedure - essential in environmental heavy metal analysis - has to be carried out with two different cells, one without and one with standard addition.

This may cause gross errors in the analysis at low levels. In this report we describe a method to improve the standard addition procedure by automatical addition of one or two spikes of standard solution to the sample cell from a buret.

If, using this method, both high and low peaks are recorded it is convenient to use a new sheet of paper after each scan. A scheme is presented here to change the paper advance control.

The use of a rotating disc electrode (RDE), especially the Glassy Carbon Mercury Film Electrode (GCMFE or GCE) results in a higher sensitivity and a better resolution of the copper peak than a HMDE. The incorporation of a rotating GCE (after ref. 1) is given. All electronic changes are designed that, if needed, the old situation is restored easily.

The standard procedure for calculation of the concentration may easily lead to incorrect determination of the concentration. Especially in environmental samples, the baseline may change, thus disturbing the calculation. This causes the need of manual calculation of the results.

The high consumption of (pure) nitrogen is expensive, moreover, it may cause N_2 shortage when the analyzer is used in the field (e.g. on board ship). Proposals are made to reduce the consumption of nitrogen.

When heavy metals in natural (seawater) samples are analysed for speciation- or complexing capacity studies, the pH should be controlled without the addition of a buffer solution. The design of a pH-stat, using CO_2 gas as reagent is described.

Acknowledgements.—We are gratefull to Mr. J. van Heerwaarden for his technical assistance, and to Mr. J.C. Duinker for his usefull comments on the manuscript.

II. APPARATUS

The analytical system - (PAR model 374) includes a model 300 Console (Polarographic Analyzer) and a model 316 Automated Cell Sequencer. The original HMDE was replaced by a model 303 Static Mercury Drop Electrode (SMDE)(E.G. & G.). The automated buret, incorporated in the system is a Reagenz Dosierer model 5211 (Eppendorf). The pH-stat consists of a pH meter model 632 and an Impulsomat E 473 (Metrohm). This combination controls a solenoïd valve type 117A (Bürkert). For the rotation of the Glassy Carbon Electrode we used a synchronous motor model SY 52×60-4 (Dunker Motoren).

III. TECHNICAL ASPECTS

A. Standard addition from an automated buret

The method of standard addition requires the addition of one or more spikes of a standard solution to the sample. We have avoided changes in the computer program (EPROM) and we have used the "replications" lights on the console as a steering command. When after the sample scan, the replications light jumps from 3 to 2, a pulse is generated, triggering the buret. A scan is made and when the light jumps from 2 to 1 a new spike is added and another scan is made. The spikes may range from 10 to 1000 µl by the use of different cylinders with the buret. The polythene tubing from the buret (2 × 1 mm Ø) enters the cell through a hole that was drilled in the electrode support block. A problem was the entry of the standard solution in the sample. Ending of the tube above the sample gave irreproducible results, due to irregular drop formation at the end. Dipping the tube in the solution gave errors due to leakage and diffusion of standard solution into the sample. Fig. 1 shows the

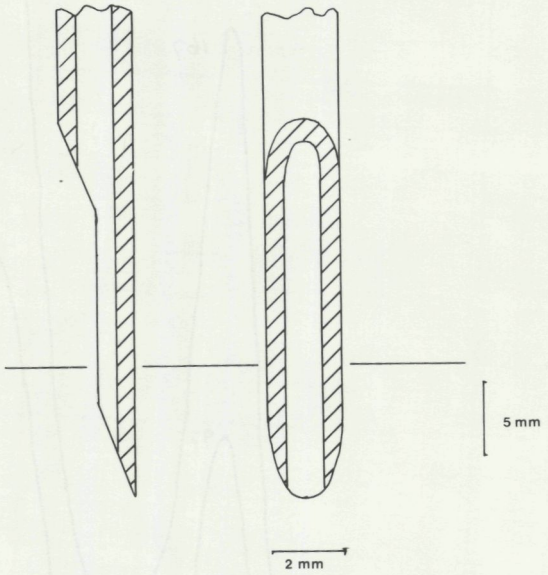


Fig. 1. Design of the tip of the standard addition tube. In order to obtain a plain view the diameter is exaggerated.

end of the tube, cut under a sharp angle. The tip of this point is immersed in the sample, the surface tension of the solution will ensure a reproducible addition. The drop does not grow, but it glides down along the tip. Only a very small drop of standard solution will remain at the end of the tube. When the height of the tip is carefully chosen, the reproducibility of the analysis is within 10 %, at nmol/1 level. Fig. 2 gives an example of a voltammogram, sample and two standard additions of cadmium, lead and copper (0.445, 4.83 and 15.7 nmol/1 respectively).

A schematic diagram of the Pulse Shaper for the automated buret in combination with the PAR 300 is given in Fig. 3. Only the lamps 3 to 2 and/or 2 to 1 (in down counting sequence) are allowed to activate the automated buret. The 74221 IC gives a positive pulse with a length of "t" on a

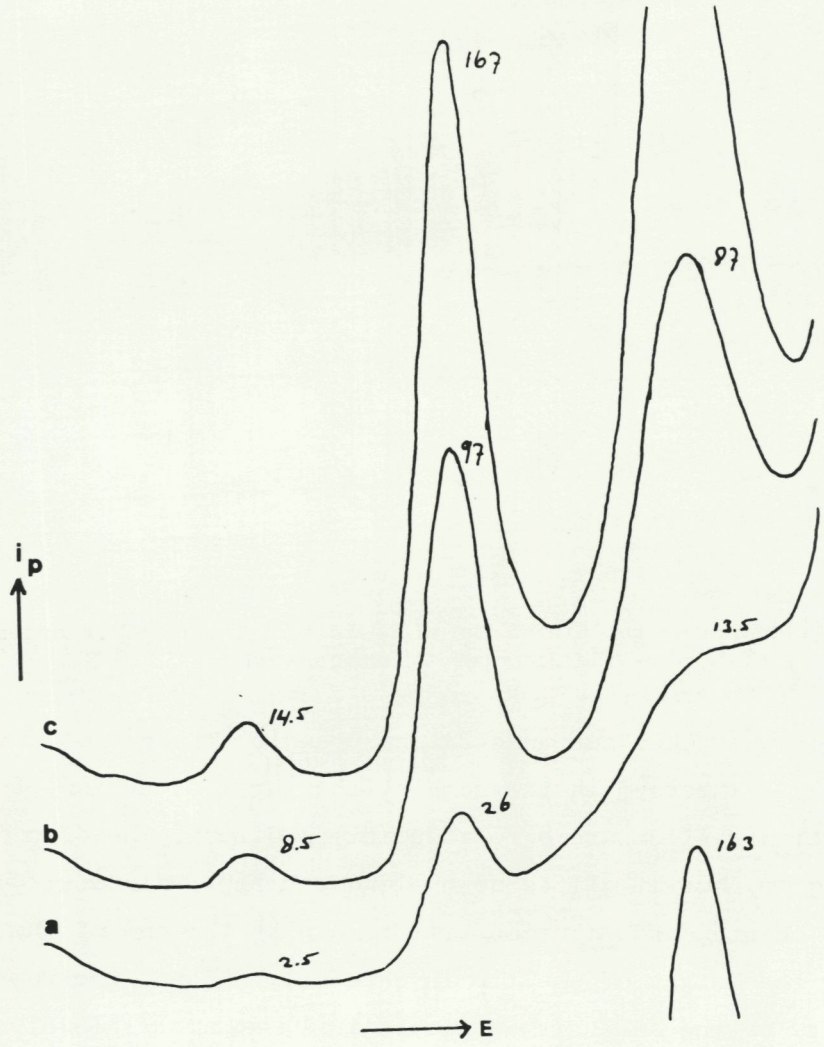


Fig. 2. Voltammograms representing a seawater sample scan (2), and two subsequent standard addition scans (b and c). Peak height in mm. Calculated concentrations: cadmium 0.031 ppb, lead 0.32 ppb and copper 0.36 ppb (0.27, 1.5 and 5.6 nmol/1 resp.).

negative transition of lamp 3 (or 2) control pulse from IC "U 61" on the Display Board (ref. 2; pVII - 26). A logic "$\overline{\text{AND}}$" with the pulses of lamp 2 (or 1) results in a closure of the reed relay contacts. The length of the contact

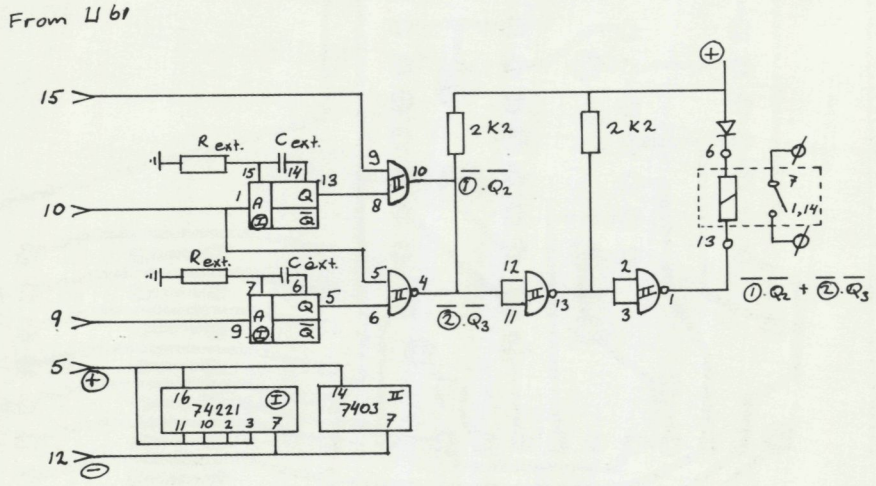


Fig. 3. Schematic diagram of a Pulse shaper for the automated buret-PAR 374 combination: R_{ext} = 2 K - 40 K; C_{ext} = 10 pF - 100 µF.

closure is determined by the R - C combination and follows the expression R × C × ln 2 in seconds. The value limits are:

$$2\ K < R < 40\ K$$

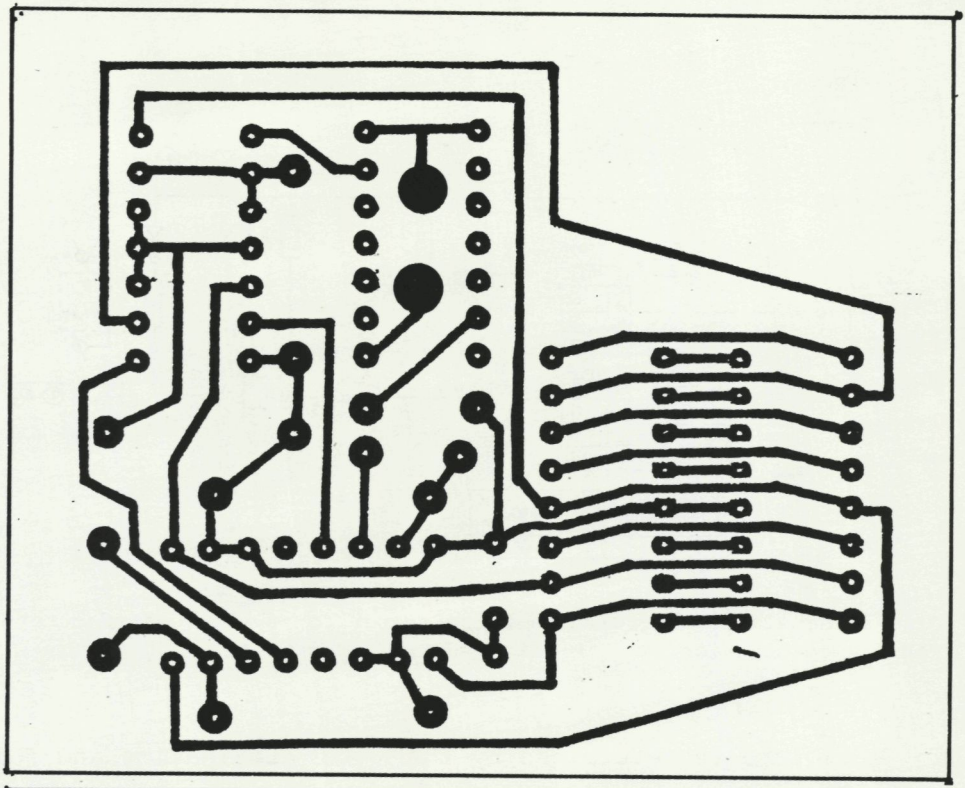
$$10\ pF < C < 100\ \mu F$$

The print design and the parts location diagram are shown in Fig. 4. To achieve the possibility to return to the original situation a plug is soldered to the print, which is put in "U 61" on the Display Board, the 7475 IC is connected to the new print. The buret is connected to the system through a coax cable.

B. Paper advance control

The increase of peak height causes the need of paper transport between the sample and the standard addition scans.

When the buret is activated, current flows through the optocoupler on the Paper Advance Board (Fig. 5). This



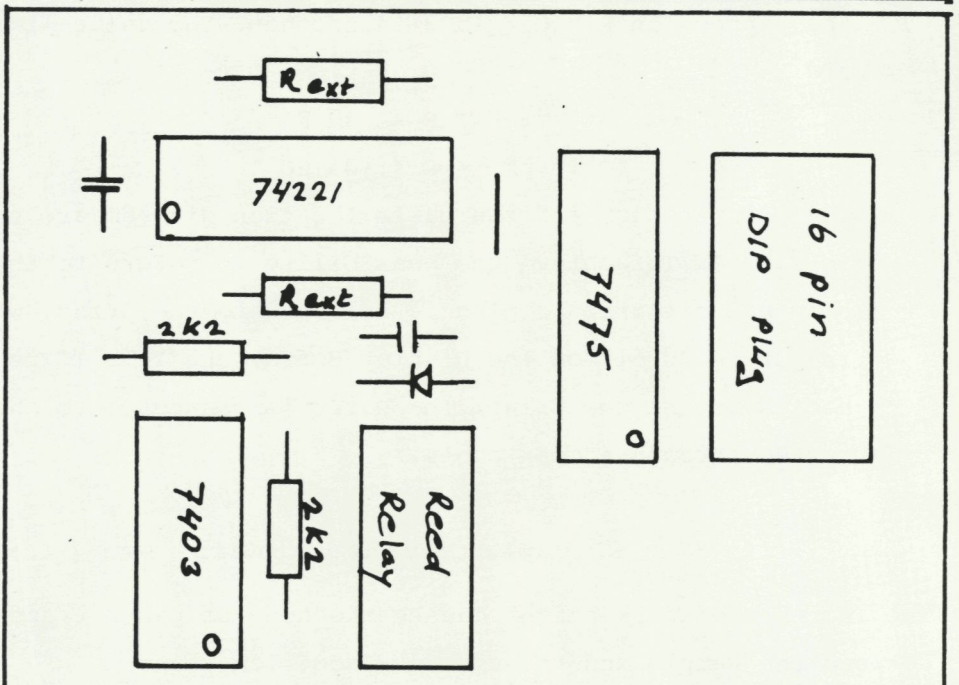


Fig. 4. Pulse shaper for automated buret-PAR 374 combination (scale 2:1). a, Print design, copper side. b, Parts location diagram.

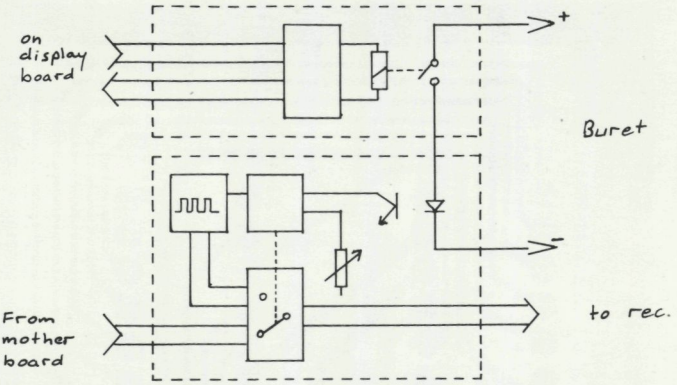


Fig. 5. Function diagram of the automated buret/paper advance system.

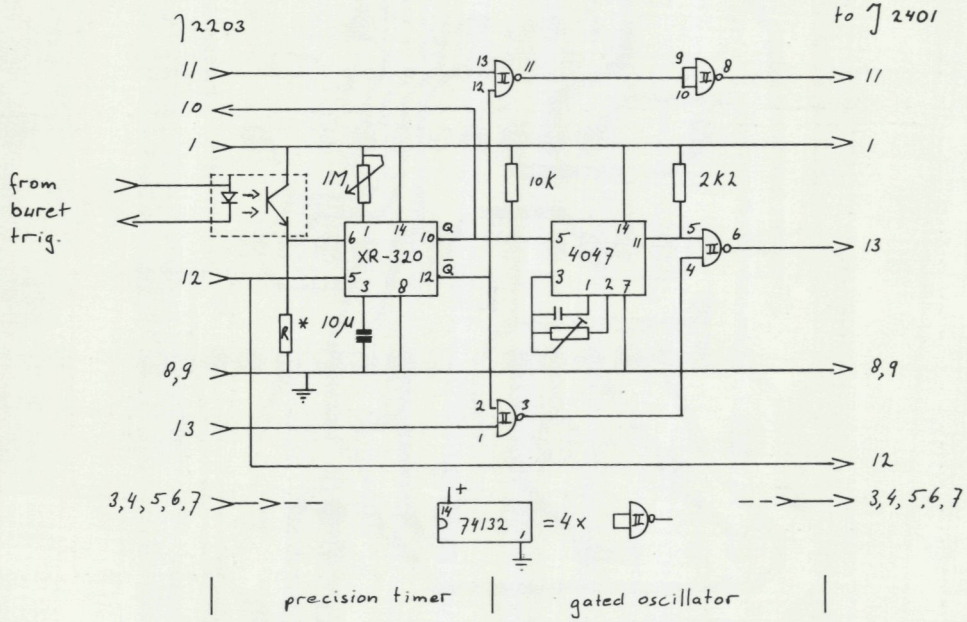


Fig. 6. Paper advance control circuit for PAR model 300. * R depends on the type of optocoupler.

triggers the timer of which the "ON" time is controlled by a potentiometer. The timer disables the plotter digi-

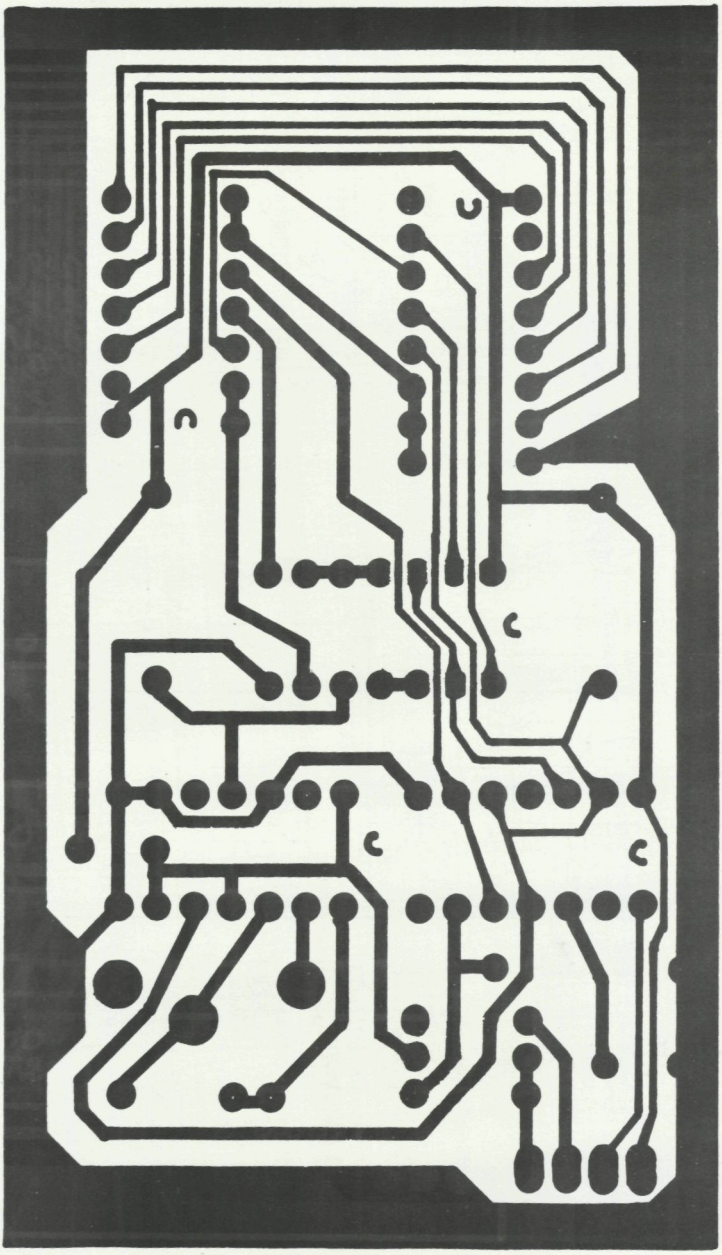
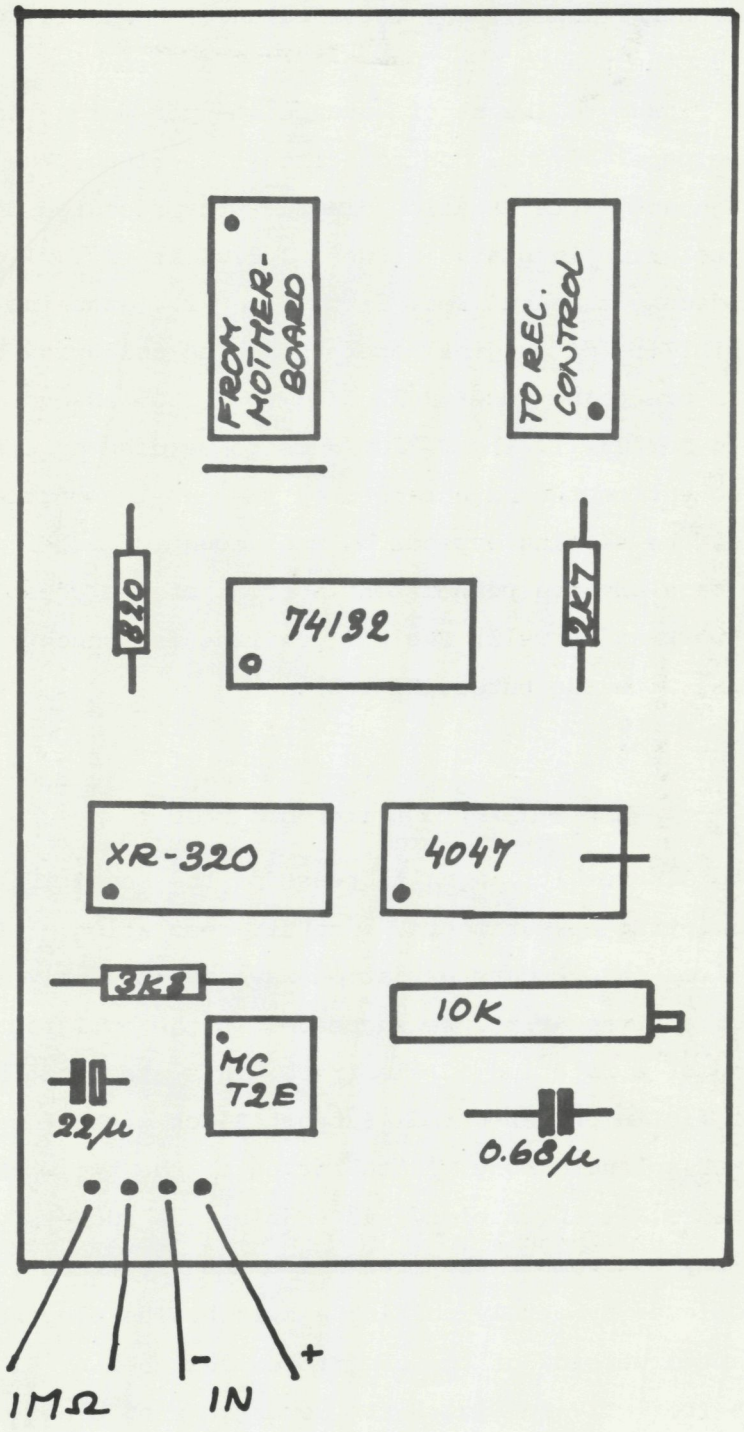


Fig. 7. Paper advance control for PAR 300 (scale 2:1). a, Print design, copper side. b, Parts location diagram.


FROM MOTHER-BOARD
TO REC. CONTROL
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74132
2K7
XR-320
4047
3K3
10K
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tal control lines (pen, motor advance, - enable, etc.), forces the pen to the "UP" position and sends a square wave signal to the paper advance stepper motor. In Fig. 6 the paper advance control circuit is given, the print design and parts location diagram are presented in Fig. 7. The print is placed between J 2203 and J 2401 on the Interconnect Board (ref. 2; p VII - 22), ensuring the possibility of original operation. The following connections are to be made: J 2203/13 to J 2205/10 and J 2204/13 to J 2203/11. The J 2201/6 is to be disconnected. A 1 MΩ potentiometer is attached on the outside of the console, the setting depends on the amount of paper advance. The page advance pushbutton in front of the console is now working as well. The trigger line is connected in serial with the buret (Fig. 5).

C. Incorporation of a GCE

A rotating GCE results in an increase of the sensitivity of the voltammetric measurements, a better resolution of the copper peak from the mercury oxidation wave and possibly in a reduction of analysis time. We succeeded in the building and installation of a rotating GC electrode. This electrode is designed to fit in the Electrode Support Block without removal of the SMDE solenoïd body. Installation of the two working electrodes is also possible. This enables the successive analysis of any one sample with two different electrodes, which can be achieved by merely pulling a switch. The electrode design is an adapted version of the electrode published by SIPOS, MAGJER & BRANICA (ref. 1). In Fig. 8 the demensions of electrode and

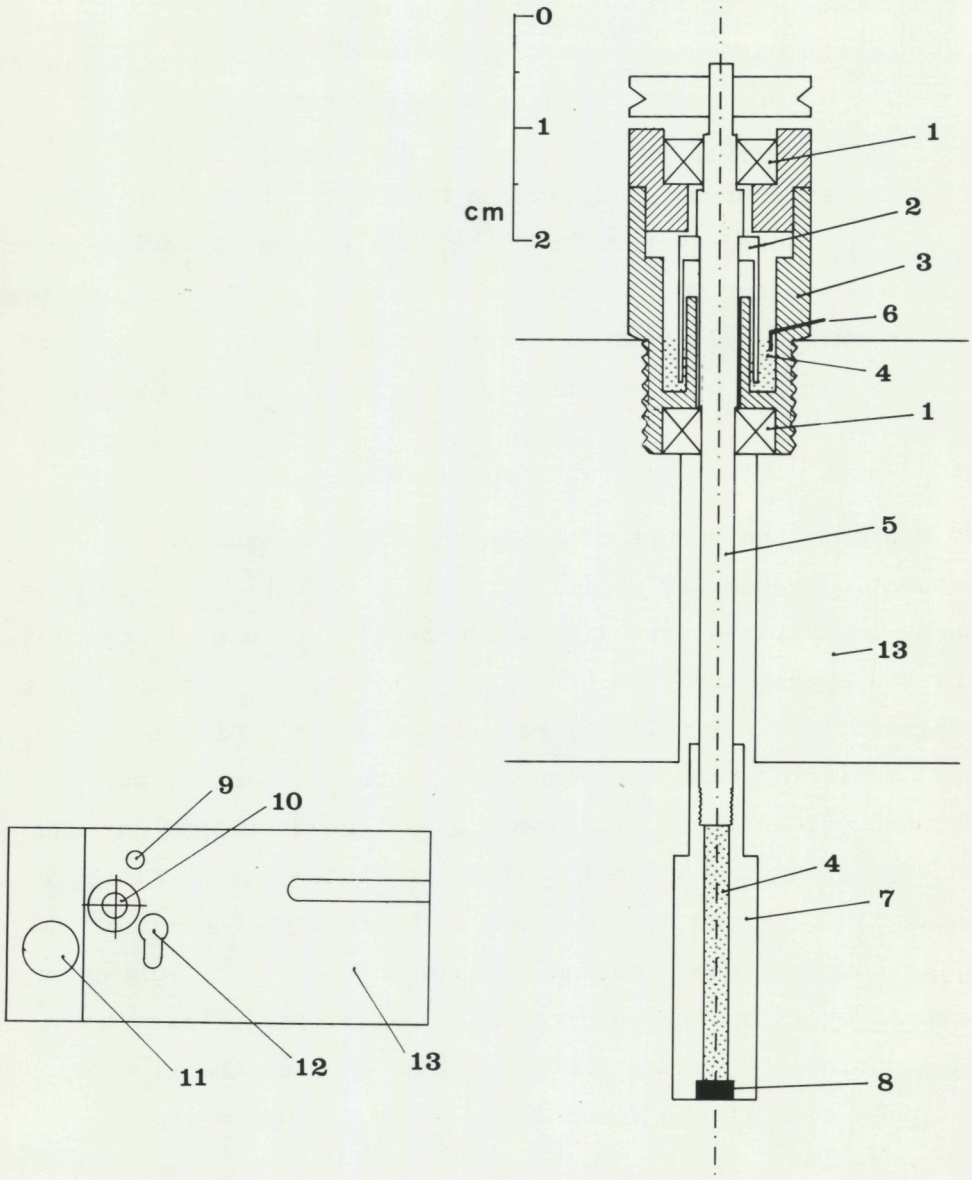

Fig. 8. Design and dimensions of the rotating GCE (a) and the electrode support block (b): 1 ball bearing, 2 stainless steel bell, 3 electrode housing, 4 mercury, 5 stainless steel shaft, 6 platinum wire, 7 telfon electrode tip, 8 glassy carbon, 9 counter electrode, 10 GCE, 11 reference electrode, 12 SMDE and 13 electrode support block.

Electrode Support Block are given. For the rotation we used a synchronous motor at 1500 rpm, attached to the carriage. A small part of the base cover had to be removed (Fig. 9).

The motor is connected to a solid state relay, with use of the main power source. The steering is parallel to the stirrer override, using U 4503/11 of the Control Panel Board (ref. 3; p V - 8) and common. An extra switch may put the GCE out of function when the SMDE is in operation. The platinum wire contact on the GCE is connected to Pin E 2 on the Interface Board (ref. 3; p V - 15).

D. Nitrogen supply

To minimize the amount of N_2 in running the analyzer, the pneumatic system was modified to allow operation by air pressure. The air pressure line was connected to the nitrogen entry via a pressure regulator (20 psi). The exit of the input manifold (ref. 3; p I - 6) was closed and the "input gas to head manifold" line was connected to the N_2 source, set to about 5 psi as it is also used to put the destilled watertank under pressure. A solenoid valve was fitted in the nitrogen input line, driven by the reset light to stop the N_2 stream after completion of the analysis (when the reset light goes on). An override switch gives the possibility of proper operation during the set-up procedure, and ensures the flow of nitrogen even if the reset light is on, if necessary.

E. Control of pH

In studies of speciation or complexation phenomena in natural waters, existing equilibria in the sample should remain unchanged. Addition of buffering agents to the sample for con-

trolling a constant pH should be avoided therefore. Purging the sample with nitrogen before the measurement forces the O_2 as well as the CO_2 out, causing a slight increase of pH. A pH-stat using CO_2 gas as reagent offers an elegant and efficient solution to this problem. This has been carried out as follows.

> A pH electrode is immersed in the sample and connected to the impulsomat/pH meter combination which can be used as a pH-stat. The instrument gives a pluse with a length "t" depending on the difference in pH between the reading of the pH meter and the preset pH. The pulse is used to trigger a mini solenoïd valve, controling a CO_2 gas stream. To ensure a minimal amount of CO_2 bubbles per pulse, small diameter tubing is used. A needle valve is incorporated for fine adjustment.

This pH control system is used with a PAR 174/315 combination polarographic analyzer with a 25 ml cell. The pH can be controlled within ± 0.02 pH unit.

IV. CONCLUSION

The changes in the polarographic analysis system PAR 374 are an improvement to the analysis. Standard addition is carried out in the same cell, two additions are possible. The incorporation of a rotating GCE enlarges the sensitivity and resolution, the analysis time is shortened. A double amount of samples in the cell sequencer is possible. An addition of a pH-stat to an electroanalytical system ensures a constant pH during speciation measurements with minimal chance of contamination.

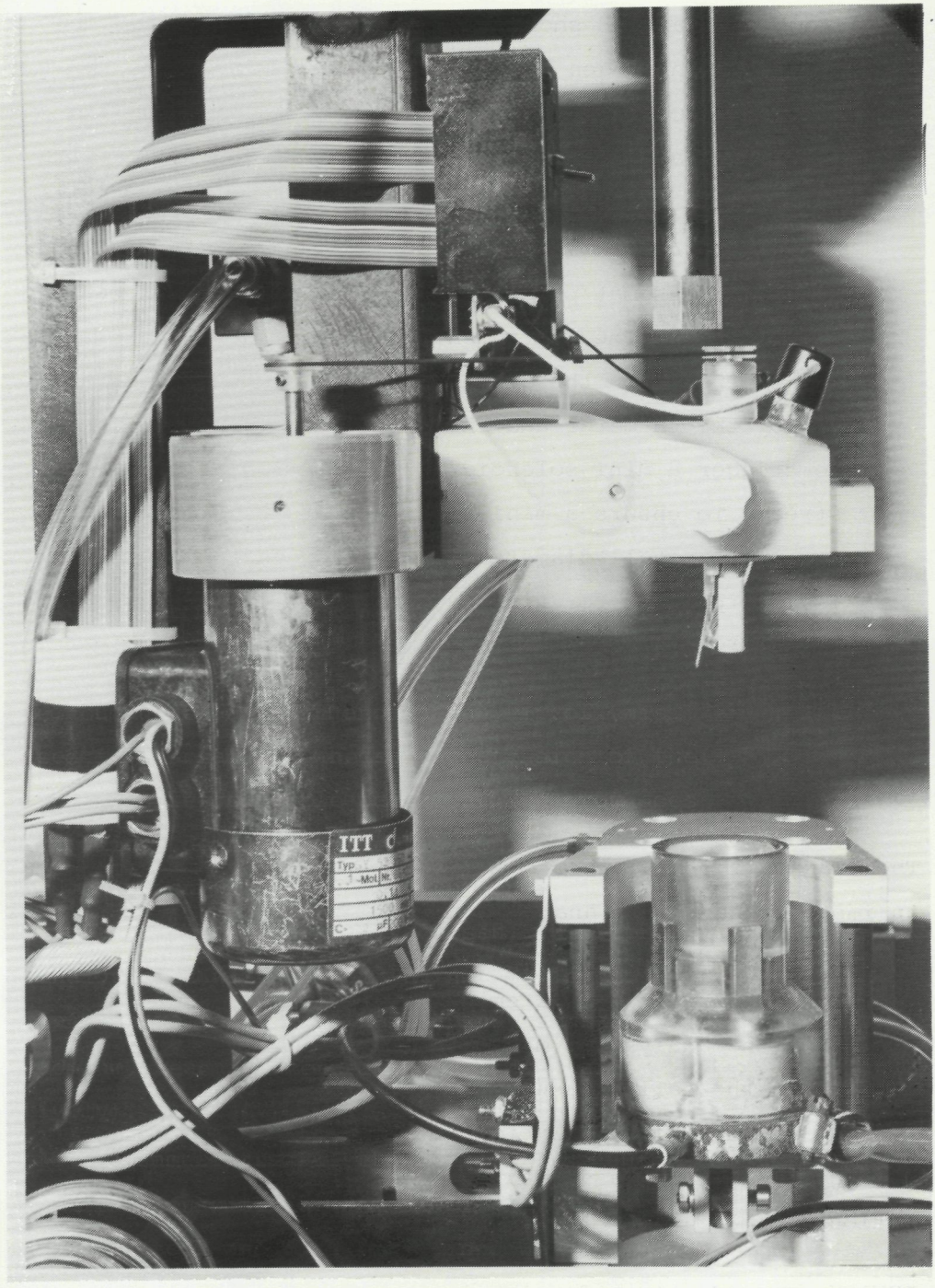

Fig. 9. Attachment of the synchronous motor and the rotating GCE to the PAR 374.


DISPOSE
ENABLE
ON
OFF

V. REFERENCES

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