POLAROGRAPH OPERATING AT THE SECOND HARMONIC OF THE ALTERNATING CURRENT

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When a small alternating voltage is applied to a polarographic cell, a whole series (spectrum) of frequencies (harmonics) appears in the cell current; these are due to the nonlinear properties of the electrode processes at the potentials of the electrochemical reactions. In ordinary ac polarography the main signal from the cell is the first harmonic, which gives a polarogram having the form of the first derivative of a classical polarogram. If we separate any particular harmonic out from the cell signal, we obtain a signal varying with electrode potential in the same way as a derivative of the order of the harmonic in question.

The advantages obtained by using the second harmonic include the possibility of securing a greater resolving power of the polarographic method and reducing the level of the capacitive current [1].

The increase in resolution between ions of similar reduction potential arises from the fact that the polarogram consists of two peaks; the width of these is roughly half the width of the peak corresponding to the fundamental frequency. Each of the peaks is proportional to the concentration. Hence for two ions of similar reduction potential any determination may be carried out by reference to peaks of different polarity.

The increase in sensitivity may be attributed to the lower level of the capacitive current, since for a fairly small amplitude of the superposed voltage the nonlinearity of the differential capacity of the double layer is very slight, particularly in the range of potentials more negative than the electrocapillary maximum.

Experiments showed that, for the ordinary base electrolytes used in polarography, the ratio of the useful signal to the signal of the capacitive current is an order higher on working at the second harmonic than at the fundamental frequency.

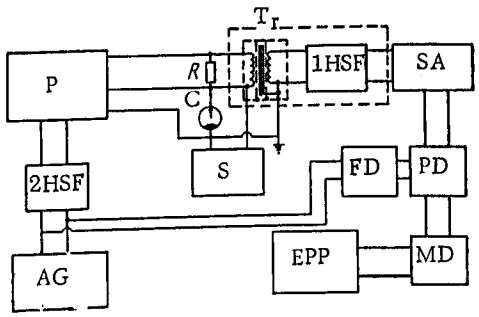

Fig. 1. Block diagram of a second-harmonic ac polarograph: P = potentiostat, R = measuring resistance, C = cell, Tr = transformer, 1HSF = first harmonic stopping (blocking) filter, SA = selective amplifier, S = synchronizer, PD = phase detector, AG = audio generator, EPP = EPP-type automatic recorder, MD = memory device, FD = frequency doubler, 2HSF = second harmonic stopping filter.

When using the second harmonic, it is essential to ensure good separation of the latter from the whole of the remaining frequency spectrum, and primarily from signals of the fundamental (ground) frequency, the amplitudes of these being an order higher. The problem of filtering the second harmonic is executed by the polarograph amplifier. Stopping of the fundamental frequency is best effected at the amplifier input, since in the course of signal amplification nonlinear distortions are inevitable. The distortion is still further exacerbated by the fact that the signal of the capacitive current at the ground frequency is greater than the dynamic range of the amplifier at the required amplifications.

The ac voltage applied to the cell should also be filtered off from the second harmonic.

The phase detector executes the usual functions of cutting off the capacitive current. However, as a result of

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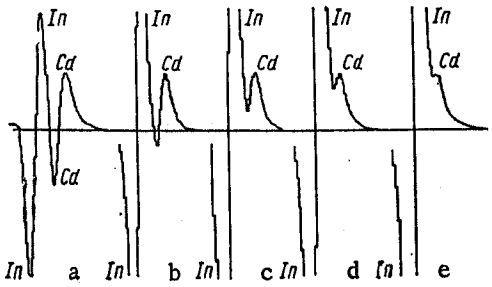

Fig. 2. Second-harmonic polarograms of a solution of In and Cd with a base electrolyte of 6-M HCl for In : Cd ratios of a) 1 : 1; b) 5 : 1, c) 15 : 1; d) 10 : 1; e) 20 : 1.

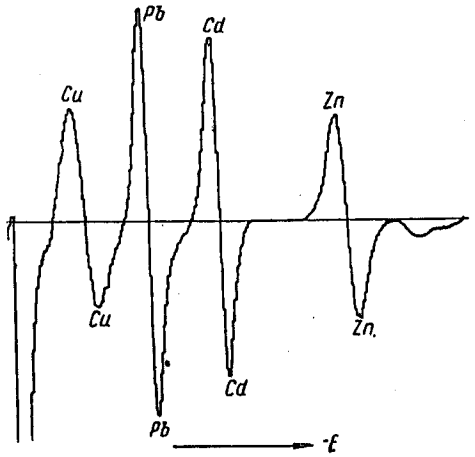

Fig. 3. Second-harmonic polarograph of a many-component solution of Cu, Pb, Cd ($1 \cdot 10^{-6}$-M) and Zn ($5 \cdot 10^{-6}$-M) with a base electrolyte of 1-M KCl.

the fact that the signal being analyzed has a double frequency, a control voltage of the same frequency must be supplied to the detector.

Figure 1 shows a block diagram of a second-harmonic polarograph. The main units (except for the amplifier) are the same as in an ordinary ac polarograph. Only the frequency-doubling unit is new.

Filtration of the second harmonic is achieved by means of the blocking (stopping) filter 1HSF based on a T-type RC filter circuit.

By way of amplifier, a selective microvoltmeter of the V-6-2 type, tuned to the second-harmonic frequency, is employed. In order to ensure the better removal of the ground frequency, a blocking filter is placed in the amplifier between the stages based on the second half of the L-5 and L-6 tubes.

Thus, by tuning the amplifier to the frequency of the second harmonic (in our case 120 cps) and tuning the blocking filters to the ground frequency (60 cps), the ground frequency may be weakened by 54 dB relative to the second harmonic. The maximum current sensitivity of the measuring part of the apparatus is $\geq 10^{-9}$ A/division.

The phase detector is supplied through a frequency doubler based on the circuit of a two-half-period rectifier with a filter tuned to the second harmonic. The rectifier and filter are separated by a tube buffer stage.

The considerable gain in the resolving power of the device facilitates analysis in those cases in which no analysis can be achieved with ordinary ac polarographs.

Figure 2 shows the polarograms of In and Cd with a base electrolyte of 6-M HCl for various concentration ratios. As the In : Cd ratio increases the negative peak becomes more and more fogged, but only beginning from a ratio of 10 : 1 is the positive peak affected. Even for a ratio of 20 : 1 this is distinguished better than the peak obtained for a concentration ratio of 5 : 1 in an ordinary ac polarogram. Thus in the present case the resolving power improved by no less than a factor of four. This advantage is of decisive value, for example, when analyzing semiconducting materials containing indium and cadmium.

Figure 3 shows the polarogram of a many-component solution.

LITERATURE CITED

1. H. H. Bauer, J. Electroanalyt. Chem., 1, 256 (1959-1960); D. E. Smith and W. H. Reinmuth, Anal. Chem., 33, 482 (1961).