We have received a number of inquiries concerning manufactured polarographic apparatus and the suitability of particular types of instruments for the solution of analytical problems.

At our request, these questions are being answered here by workers of the chemical laboratory of the Central Research Institute for Ferrous Metallurgy.

INSTRUMENTS FOR POLAROGRAPHY

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Translated from Zavodskaya Laboratoriya, Vol. 28, No. 11, pp. 1398-1400, November, 1962

Photographic recording polarographs offer considerable advantages due to their simplicity; they are the main types of polarographic apparatus used in many production and industrial research laboratories. Our industry produces the PA-1 photorecording polarographs [1]. The widely used photorecording instruments at the present time are: the improved Heyrovsky LP-55 polarograph [2] and the Heyrovsky M-102 micropolarographs [3].

In recent years photorecording instruments have been replaced by electronic automatic recording polarographs in which the galvanometers are replaced by electronic tracking devices.

The electronic integral-differentiating polarograph TsLA-PE-312 developed by Tsfasman and Benevol'skii has been well received [1, 4]; it has high sensitivity (10^{-5} mole/liter of material). The instrument is not sensitive to vibration and it can therefore be used under plant conditions. The industry is now producing a modified TsLA polarograph under the designation PA-2.

Of the electronic automatic recording instruments designed abroad the most interesting is the Kelley and Milner polarograph [1, 5]. It is intended for the analysis of radioactive materials, where it is essential to use a micropolarograph since the volume of the solutions is less than 0.1 ml, or for the analysis of dilute solutions in which the effect of the capacitance current is very large. The authors have been able to correct for the capacitance current. For this purpose they used a device called a "curve repeater" which is used to subtract the polarogram of the pure background from the polarogram of the solution containing the material being analyzed. Solutions containing $2 \cdot 10^{-8}$ to $2 \cdot 10^{-7}$ mole of lead can be analyzed with a relative accuracy of ± 20%. The polarograph can be successfully used for production and research work.

As well as normal polarograms the Atlas polarograph (West Germany) can also take pulse polarograms (the voltage is only fed to the drop in the last period of its existence) [1]. The polarograph records currents between $5 \cdot 10^{-8}$ and $7.5 \cdot 10^{-5}$ A. The range of measurement of the current makes it possible to analyze solutions containing between 10^{-6} and 10^{-3} mole/liter of the analyzed material.

The RO-4 electronic automatic recording polarograph produced in Denmark has single-drop Kemula electrodes (type E-69) which makes it possible to determine $10^{-7} - 10^{-6}$ mole/liter of analyzed material or less.

Oscillographic polarography has been developed in recent years.

The TsLA oscillographic polarograph [1, 6] has been developed and is now being produced by the Rostov experimental plant. It can take polarograms in the coordinates i-E; di/dE − E; i-t.

It is possible to observe polarograms on the screen of a cathode-ray tube and to photograph them with a photographic attachment. Using the TsLA oscillographic polarograph the polarography can be conducted on mercury electrodes and electrodes of other materials. The initial polarizing voltage is between + 1 and − 2 V. The amplitude of the linear change in voltage can be between 0 and 3 V. The sensitivity of the instrument (for cadmium) is 10^{-6} mole/liter, the resolving capacity for the determination of cadmium in the presence of copper is 5,000. During the preliminary electrolysis of substances forming an amalgam, the sensitivity of the instrument is increased to 10^{-8} mole/liter. The instrument is intended for the analytical control of small contents of elements and also for the investigation of electrochemical and physicochemical processes.

In 1959 Ya. P. Gokhshtein and co-workers [7] developed a new model of an oscillographic polarograph for the determination of substances with a content of $1 \cdot 10^{-7}$ to $1 \cdot 10^{-3}$ mole/liter. This polarograph uses a circuit which permits the use of both periodic and single scanning with various fixed rates of change in potential. This made it possible to use a dropping mercury electrode, a stationary mercury electrode and solid electrodes. The use of a stationary mercury electrode, having a surface which was 200-300 times greater than the surface of the mercury drop, increased the sensitivity of the method to $1 \cdot 10^{-7}$ mole/liter.

A Comparative Evaluation of the Sensitivity and Resolving Capacity of Various Types of Polarography

Types of polarography	Sensitivity, mole/liter		Resolving capacity
	reversible processes	irreversible processes	
Classical	10^{-5}-10^{-6}	10^{-5}-10^{-6}	100-200
Oscillographic	$5 \cdot 10^{-7}$	$5 \cdot 10^{-7}$	400
Alternating current	$1 \cdot 10^{-7}$	$2 \cdot 10^{-6}$	2000
Pulse	10^{-8}	10^{-8}	2000

The GEOKhI oscillographic polarograph is now being produced in the form of the model OP-1-61 [8] with a new system of synchronization, ensuring automatic renewal and removal of the stationary drop electrodes, which makes it possible to work with and without accumulation. When operating without accumulation the sensitivity of the instrument is 10^{-7} mole/liter and when working with accumulation it is 10^{-9} mole/liter. The instrument includes an electrolytic cell with automatic renewal of the stationary electrode.

In Czechoslovakia the national company "Krizik" is producing an electronic polaroscope – a portable instrument for oscillographic polarography with a set current, making it possible to obtain curves in the coordinates dE/dt – E [9. 10].

A comparative evaluation of certain trends in polarography is given in the table, taken from the paper by S. B. Tsfasman [11].

As can be seen from the table, alternating current and pulse polarographs have high sensitivity. The most highly developed and sensitive alternating current polarograph is the Mervyn-Harwell square-wave polarograph, designed by Barker [12] and now produced in Britain.

The instrument has very good analytical characteristics and its sensitivity is 200 times that of the classical polarographs. It can be used to determine concentrations of substances below $1 \cdot 10^{-5}$ g. The high resolving capacity of the instrument means that little chemical preparation of the sample is necessary.

The instrument has found extensive practical use abroad [13-17]. In the Soviet Union a square-wave polarograph has been used for the analysis of nonferrous metallurgical products [18, 19].

In order to use an alternating current polarograph for the continuous control of production solutions, S. B. Tsfasman and co-workers [1, 20] have developed a polarographic continuous concentration measurer, based on polarography using an alternating sine current. The instrument can also be used as an alternating-current polarograph. When the instrument operates as a concentration measurer it uses a thermostatically controlled polarographic cell through which the solution in question flows continuously. The resulting polarograms represent the dependence of the active component amplitude of the alternating current on the constant voltage on the cell.

When the instrument is used as an alternating-current polarograph the receiver is the usual apparatus for conducting polarographic analysis under laboratory conditions.

The prototype of the polarographic concentration measurer was tested under the production conditions of the "Elektrotsink" plant. The zinc electrolyte, having been subjected to purification to remove copper and cadmium, was checked for the content of remaining cadmium impurity. While the instrument was operating in the plant, comparative data were obtained for the instrument readings and laboratory analyses. The differences did not exceed ± 4%.

Gorelkinskii, Grinman and Kozlov [21] proposed an alternating-current polarograph with a phase-sensitive bridge, intended for the large-scale analysis of ore materials.

It therefore follows that the TsLA-PE-312 electronic polarograph is the most suitable for the determination of elements in metals, steels and alloys (containing $1 \cdot 10^{-3}$ to 3-5% of the element).

The TsLA oscillographic polarograph and the GEOKhI brand OP-1-61 oscillographic polarograph are recommended for the determination of ultrasmall amounts (from $1 \cdot 10^{-8}$ to $1 \cdot 10^{-4}$ %).

The most highly developed foreign polarograph, which can determine ultrasmall amounts of substances in the presence of interfering elements in metals, steels and alloys is the Mervyn-Harwell square-wave polarograph. Czech polarographs are sensitive and completely reliable for the production analysis of ores, metals, steels, and alloys.

LITERATURE CITED

1. S. B. Tsfasman, Electronic Polargraphs [in Russian]. Metallurgizdat, 64-79, 100, 126, 146 (1960).
2. J. Heyrovsky, The Technique of Polarographic Investigation [Russian translation]. IL (1951).
3. T. A. Kryukova, S. I. Sinyakova, and T. V. Aref'eva, Polarographic Analysis [in Russian], Goskhimizdat, 599 (1959).
4. S. B. Tsfasman, Zavodskaya laboratoriya, XX, 8, 977 (1954).
5. M. T. Kelley and H. H. Milner, Anal. Chem., 24, 1895 (1952).
6. The TsLA oscillographic polarograph, Zavodskaya laboratoriya XXVIII, 4, 519 (1962).
7. Ya. P. Gokhshtein, A. F. Volkov, S. V. Kuz'min, and V. A. Yanchevskii, Zavodskaya laboratoriya, XXV, 8, 1008 (1959).
8. The OP-1-61 oscillographic polarograph, Zavodskaya laboratoriya, XXVIII, 4, 518 (1962).
9. R. Kalvoda, Die Pharmazie, 11, 101 (1956).
10. J. Heyrovsky, Anal. Chim. Acta, 12, 600 (1955).
11. S. B. Tsfasman, Zavodskaya laboratoriya, XXVI, 9, 1064 (1960).
12. G. C. Barker, and J. L. Jenkins, analyst, 77, 920, 685 (1952).
13. D. J. Ferrett, G. W. C. Milner, and A. A. Smales, Analyst, 79, 945, 731 (1954).
14. D. J. Ferret and G. W. C. Milner, Analyst 30, No. 947, 132 (1955).
15. D. J. Ferrett and G. W. C. Milner, Analyst. 81, No. 961, 193 (1956).
16. G. W. C. Milner and L. J. Slee, Analyst, 82, No. 972, 139 (1957).
17. D. J. Ferrett, G. W. C. Milner, H. O. Shalgosky and L. J. Slee, Analyst, 81, 966, 506 (1956).
18. R. G. Pats and S. B. Tsfasman, Zavodskaya laboratoriya, XXVII, 3, 266 (1961).
19. R. G. Pats, Zavodskaya laboratoriya, XXVIII, 1, 18 (1962).
20. S. B. Tsfasman, I. E. Bryksin, and B. S. Bruk, Zavodskaya laboratoriya, XXIV, 11, 1409 (1958).
21. Yu. V. Gorelkinskii, I. G. Grinman, and G. S. Kozlov, Zavodskaya laboratoriya, XXVI, 9, 1141 (1960).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. ***Some or all of this periodical literature may well be available in English translation.*** **A complete list of the cover-to-cover English translations appears at the back of this issue.**