MODERN ELECTRONIC POLAROGRAPHS

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In recent years three basic directions have stood out in the development of polarograph design: the creation of instruments for analytical application, for scientific research, and for production control.

Instruments for analytical tasks must possess high sensitivity and resolution. With modern instruments of high sensitivity one can determine reversibly reducible components in concentrations of 10^{-7}-10^{-8} M at a mercury drop electrode. With simple instrumental methods one cannot pick out such low signals from a background of interferences which are thousands or tens of thousands of times larger than the signal. This introduces considerable complications into an instrument.

The broadening range of problems to be solved in analytical practice and the complexity of the analytical starting materials have necessitated the introduction of new working modes, e.g., the three-electrode regime, a larger selection of scan rates, the introduction of scan reversal, etc.

The basic trend in the development of polarographs for scientific research is the creation of universal, multipurpose instruments. Their basic feature is universality: the availability of many working modes, the adoption of special means to stabilize the polarizing tension and zero current, and the introduction of accurate control of the polarizing tension.

For the solution of problems in industrial control, reliable instruments are required which are simple to adjust and operate, and do not require a highly skilled operator. It is of special value to develop a sensor which is capable of functioning normally with process solutions under industrial conditions, for example one with automatic sample preparation and mercury purification.

The need for a profound study of the mechanism of a process in order to obtain analytical data, and the investigation of electrochemical processes at a very low level of the signals often obliterate the boundary line between instruments of the analytical and research level.

The polarographic instrumentation in the USSR is developed by a number of organizations: the VNIIAchermet (All-Union Scientific-Research Institute of Automation of Iron Metallurgy), the VNIKItsvetmetavtomatika (All-Union Scientific-Research and Design Institute of Automation of Nonferrous Metallurgy) (Moscow), the Rostov Test Plant (Rostov-on-Don), the Frunze "Fizpribor" Plant (Frunze), the VNIINauchpribor (All-Union Scientific-Research Institute of Scientific Instruments) (Leningrad), and also by Chairs of the Kazan Aviation Institute, the Tomsk Polytechnic Institute, and the Laboratory of Measuring Techniques of the Academy of Sciences of the Moldavian SSR.

The main technical data of polarographic equipment are given in Table 1. They are drawn from advertising material and literature sources (Note: vector = phase-sensitive ac. Transl.).

Mass-produced are: the ac polarograph PPT-1, the oscillopolarograph PO-5122, models 02 and 03, and the automatic electronic polarograph PA-3. The other instruments exist as prototypes or are about to come out of the development stage and are ready for mass production: the universal electronic polarograph UPÉ-6124, the high-frequency polarograph PL-2, the laboratory polarograph PL-1, and the building-block polarograph UNIPOL-1.

Inspection of the technical data shows that in our country there exists a large number of instruments which cover all modern directions of the development of the polarographic method.

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TABLE 1. Domestic Polarographs and Their Technical Data

Designation and type of polarograph	Development and marketing by	Principal operating modes	Sensitivity, M
1	2	3	4
Alternating current, PPT-1 [1]	VNIIAchermet, Gomel' Plant	1) Dc; 2) Vector contin.; 3) Vector Tast 4) Class.; 5) Contr. curr. oscill., with recording of signal by recorder; 6) 3-el.; 7) Stat. electr.; 8) Tast	At DME 5×10^{-6} for reversible reactions
Universal electronic, UPÉ-6124, [1, 2]	VNIIAchermet	1) Class.; 2) Tast; 3) Osc., with recording of signal by recorder or oscilloscope; 4) Diff.; 5) Fractional diff.; 6) 2nd deriv.; 7) Stat. electr.; 8) 3-el.	At DME in oscillog. mode 10^{-6}
Detector [1, 3]	VNIIAchermet	1) AM hf; 2) Vector contin.; 3) Vector tast; 4) 3-el.; 5) Stat. electr.	10^{-7}
Oscillographic, PO-5122, model 02 [16]	VNIIAchermet, Rostov Test Plant	1) Osc.; 2) Diff.; 3) i-t curves; 4) 3-el.; 5) Stat. electr.	At DME $5 \cdot 10^{-7}$
Oscillographic, PO-5122, model 03 [3]	VNIIAchermet, Rostov Test Plant	1) Osc.; 2) Diff.; 3) Saw-tooth scan; 4) Triang. scan; 5) First drop; 6) i-t curves; 7) Class.; with recording by recorder; 8) Stat. electr.; 9) 3-el.	At DME $5 \cdot 10^{-7}$
Automatic electronic, PA-3	Frunze "Fizpribor" Plant	1) Class.; 2) Diff.	$2 \cdot 10^{-6}$
High-frequency, PL-2 [4]	VNIKItsvetmetavtomatika	1) AM hf; 2) Vector	–
Laboratory, PL-1	VNIKItsvetmetavtomatika	1) Vector; 2) For 3 elem. as programmed	10^{-6}
Building-block type, UNIPOL-1 [5]	VNIINauchpribor	1) Class. 2) Tast 3) Comp. 4) Vector contin. 5) Vector tast 6) 2nd harm. 7) Stat. electr.	At DME 10^{-5} 10^{-6} 10^{-6} 10^{-7}
Electron beam, ÉLP-7 [15]	Chair of Fundamentals of Radio Engineering, Kazan Aviation Institute	1) Contin. scann. of sweep 2) Synchr. scann. of sweep 3) Delayed scann. of sweep 4) i-t curves 5) Fract. diff.	$5 \cdot 10^{-7}$
Oscillographic, with stepped and exponential forms of polarizing voltage [6-8]	Chair of Fundamentals of Radio Engineering, Kazan Aviation Institute	1) Osc.; 2) Fract. diff.; 3) Diff.	$5 \cdot 10^{-8}$ according to [6]
Alternating current, with sinusoidal voltage and automatic compensation of bulk resistance [9, 10]	The same	1) Vector; 2) Diff.; 3) Comp. of R_{cell}; 4) Logar. reg.	10^{-9}
With amplitude-modulated sinusoidal voltage [9, 11]	Chair of Fundamentals of Radio Engineering, Kazan Aviation Institute	1) AM	$8 \cdot 10^{-9}$
Pulse oscillopolarograph with simultaneous recording of cathodic and anodic polarograms [12]	The same	1) Rect.-pulse scan for simultan. cath. and anod. polarog.;	$5 \cdot 10^{-7}$
On the second harmonic of ac [13]	Laboratory of Measuring Techniques, Academy of Sciences of Moldavian SSR	2nd harm.	–
Solid-state, direct current, PPN-1 [14]	Chair of Chemical Technology, Tula Polytechnic Institute	1) Autorepeat; 2) Osc., with recordind of the signal by oscilloscope	–

TABLE 1 (Continued)

Resolution on a concentration scale	Resolution on a potential scale, in mV	Range of starting voltage, in V	Voltage range and range of scan rates	Range of ac amplitudes, in mV	Ac frequency range	Remarks
5	6	7	8	9	10	11
At DME for Cd and Cu in ammoniacal sol. > 5000	40 at equal concn. of components determined	± 3.5	± 3 V; 1-500 mV/sec	4-40	78 Hz	A stationary mercury drop electrode (SMDE) is included in the instrument
2000	60	± 3.5	± 3 V; 1-500 mV/sec	–	–	The same
5000	35	+ 1 to −2	+ 1 -(−2V); 0.7-15 mV/sec	At double-layer capacity 4-40	Hf voltage, 6.25 kHz, 100 kHz, 1.6 MHz; modulation frequency and frequency in vector mode 50 Hz	" "
> 5000	40	+ 1 to − 2	0-(−3 V), 0.125- 16 V/sec	–	–	–
> 5000	40	+ 1 to − 2	± 3 V, 2.5-160 mV/sec and 0.25-16 V/sec	–	–	–
–	–	+ 1 to − 2	0-1 V and 0-(−2V), 5.55 mV/sec and 11.1 mV/sec	–	–	
–	–	± 3	0-3 V, 1-10 mV/sec	In op. mode 2, 32	Hf voltage 7.8 kHz, 2 MHz; modulation frequency and frequency in vector mode 38 Hz	
200	–	+ 0.5 to − 2	0-(−1.5 V, 1-3 mV/sec	30	50	
10 20	200 –		± 3 V, 0.5-50 mV/sec			
1000 5000	50 35		–	2-80	25 and 50 25	
–	–	± 2.5	± 3 V, 0.25, 0.8, 2.5, 8.0, 25 V/sec	–	–	1) Sweep is of triangular form
–	40 accord. to [6]; 45 accord. to [8]	–	to 1 V, 0.1-1 V/sec	–	–	Step height of polarizing voltage is set between 2 and 30 mV; the length is selected between 20 and 240 msec
–	45	–	± 5 V; 0.0128-3 V/min	0.1-200	20	Linear compensation of capacitance current is provided
–	40	–	± 5 V, 0.5-15 mV/sec	0-150	Carrier frequency 510 Hz; modulation frequency 20 Hz	
–	–	+ 1.5 to − 2.5	0.2-2.5 mV	Pulse amplitude 2-20	Pulse frequency 6.25-3200 Hz	
–	–	–	–	–	60 Hz	
–	–	–	± 5V, $10\text{-}10^{-5}$ V/sec	–	–	Nonlinearity of the sweep 0.1%

TABLE 2. Foreign Polarographs and Their Chief Technical Data

Designation and type of polarograph	Marketing firm	Principle operating modes	Sensitivity, M
1	2	3	4
Two-electrode, type OH-101/1	Radelkis, Hungary	1) Class.; 2) Rapid pol., with attachment OH-99.1	–
Three-electrode, type OH-102	The same	1) Class. 3-el. With attachment OH-991; 2) Rapid pol.; 3) Tast	–
Square-wave, type OH-104	" "	Dc	10^{-7}
Type LP-7	Manufacturing Enterprise for Laboratory instruments, Czechoslovakia	1) Class.; 2) Stat. Electr.	–
Polaroscope, LP-601	The same	$\frac{dv}{dt}(i)$	10^{-5}
Dc and ac, GWP-563	Institute for Scientific-Research Instruments, Academy of Sciences of GDR, Berlin	1) Class.; Vector	–
Classical, PO4	Radiometer, Denmark	1) Class.; 2) Tast with attachment DLT-1; 3) Diff.	With SMDE 10^{-6}-10^{-6}
PRG-3	Tacussel, France	1) Vector; 2) Class.; 3) 3-el.	10^{-8} (revers. process) and 10^{-6} (irrev. process)
82 P	Cambridge, Great Britain	1) Vector; 2) Contr.-curr. osc.; 3) Class.; 4) 3-el.; 5) Triang. sw.	–
Pulse, A-3100	Southern Instrument, Great Britain	1) Pulse; 2) Diff. pulse	10^{-8} (revers. process) and 10^{-7} (irrev. process)
Differential oscillographic, type A-1660	The same	1) Diff. osc.; 2) Diff.; 3) 2nd deriv.	$5 \cdot 10^{-8}$
Modification P-8	Yanagimoto, Japan	1) Class. (base model P8-A); 2) Dc sinus. (add block P8-AC); 3) Dc sq. w. (add block P8-S to P8-A); 4) Class. 3-el. (add block P8-DP to P8-A); 5) Rapid pol. (add block P8-RT)	–
Oscillographic, type PE-20	The same	1) Osc.; 2) Diff.; 3) Contr.-curr. sq. w. osc.; 4) Diff. osc.; 5) Stat. electr.	In op. mode 3 for reversible reactions $< 10^{-7}$, in op. mode 4 for irreversible reactions $< 10^{-7}$
Polarographic system	Shimadzu, Japan	1) Class. (base model RP-50); 2) Dc sinus. bridge (model BF-50); 3) Dc sq. w. (model SWP-50); 4) Correct. potent. (model AJC-50)	–
Analyzer, Model 171	Princeton Applied Research	1) Class.; 2) Vector; 3) Pulse; 4) Stat. electr.; 5) Other: pH-meter, potentiom.; 6) Diff. pulse; 7) Deriv. pulse	–
Electrochemistry system, Model 170	Princeton Applied Research	1) Class.; 2) Vector; 3) Pulse; 4) Stat. electr.; 5) Osc.; 6) Other: pH-meter, potentiom., chronopotentiom. coulom.; 7) Diff. pulse; 8) Deriv. pulse.	–
Analyzer, Model 174	The same	1) Pulse; 2) Diff. pulse; 3) Class.; 4) Tast; 5) Stat. electr.; 6) Osc.	$5 \cdot 10^{-8}$

TABLE 2 (Continued)

Resolution on a concentration scale	Resolution on a potential scale, in mV	Range of starting voltage, in V	Voltage range and range of scan rates	Range of ac amplitudes, in mV	Ac frequency range, in Hz	Remarks
5	6	7	8	9	10	11
–	–	+1-(−2)	2 V, 0.91-33.3 mV/sec	–	–	
–	–	± 2	4 V, 0.068-100 mV/sec	–	–	Can be used as potentiostat with working current 0.15 A and output voltage 100 V
5000 at a half-wave-potential difference of 200 mV	–	–	+1-(− 6V)	10-40	20	Solid-state construction; includes X-Y recorder
–	–	0-2 and 2-4	–	–	–	1) system includes stationary mercury electrode after Vogel and device for O_2 deter.
–	–	–	–	–	–	1) Voltage reading accuracy ± 1.5 and ± 3 mV
–	–	+3-(−2)	4 V	2-100	78	The signal is traced on oscilloscope screen or can be photographed with an attachment
–	–	–	+0.5-(−3V 1.66-13.3 mV/sec	–	–	1) Has linear compensation for capacitance current
–	–	–	0.02-100 mV/sec	0-500	3-3000	The system includes an SMDE; 2) Rotating platinum electrode; 3) Mechanical drop dislodgment
–	–	–	+ 2-(− 4V)	–	38	Is supplemented by an X-Y recorder and a device for drop dislodgment (drop time 0.1-100 sec)
5000 at a potential difference of 200 mV	25	–	± 2.5 V	–	–	Length of measuring pulse and pulse for cutting out capacitance current varies from 2 to 40 msec
–	100 mV in usual mode, 40 mV when recording 1st deriv., 25 mV when recording 2nd deriv.	0-2.5	–	–	–	
–	–	± 2.9	± 4 V	In mode 2: 30 In mode 3: 1-50	In mode 3: 50 or 60 In mode 3: 200	In op. mode 2, range of capacitance being compensated 0-5 μF. Op. mode 3: highest sensitivity
10000	–	+1.5-(−3.5)	0.1-1 V/sec	1-30	200	Polarizing voltage range 2 to −5 V
–	–	± 1.5	0-3V, 5 mV/sec	0-50	100	In op. mode 2, range of capacitance being compensated 0.01-1.1 μF
–	–	–	–	3-50	200	
–	–	± 5	0.15-4.5 V; 0.1-500 mV/sec	In mode 2: 0.1-10 mV	In mode 2: 25, 55, 80	Pulse length in op. mode 3: 40 msec
–	–	± 5	0.1-500 V/sec	0.1-10	10-1000	Pulse length in pulse mode: 48 msec. In the classical mode, capacitance current compensator and iR compensator provided
–	–	± 5	± 3 V, 0.1-500 mV/sec	In mode 2: 5-100		Pulse length 56 msec

Table 2 shows technical data of polarographs marketed by foreign companies. The data are drawn from company literature. Data on polarographs marketed by such well-known companies as Amel (Italy), Metrohm (Switzerland), Atlas (Fed. Rep. Germany), Sargent, and Northrup (U. S. A.) are not shown in the table because of lack of newer data on the instruments.

Polarographs from the Hungarian People's Republic, from Czechoslovakia, and Denmark are widely used in the USSR.

Great achievements can be noted in the development of domestic industrial polarographic analyzers and level indicators for continuous operation which are used in automatic control systems for concentration and composition of technical process solutions and materials.

The VNIKItsvetmetavtomatika continues to work on the development of concentration level indicators for solutions and of analyzers for solid products. The analyzer PAUN-1 and the discontinuously/periodically operating concentration level indicator PKR-1 have been constructed here [17].

The analyzer PAUN-1 is designed to carry out elementary and product (phase) analysis on solids, in particular ores, tailings, and other flotation products. It consists of a sensor with automatic sample preparation type DAUN-1 and a concentration measuring device type PIK-1. With the analyzer one can determine the copper, lead, and zinc content in one weighed sample within 20 min. Copper can be detected at a level of 0.005% abs.; the upper limit for copper and lead is 5%, for zinc it is 10% abs. The sum of the oxidized forms of lead and zinc is determined within 8 min from one weighed portion.

The concentration level indicator PKR-1 is designed for the control of technical process solutions requiring sample preparation. The instrument operates according to a program selected in the pneumatic command module KÉP-12u. Pneumatic valves serve as the functional elements of the sensor. Measuring tanks control the degree of dilution of the test solution.

The concentration level indicator "Faza 2" was developed in the North Caucasian Branch, SKBtsvetmetavtomatika (North Caucasus Bureau of Automation of Nonferrous Metallurgy). It is designed for the continuous measurement of cadmium concentration in industrial solutions of electrolytic zinc production. The range of concentrations covered is 0-10 mg/liter; the measuring uncertainty is 4%. This concentration level indicator can also be used for the analysis of other industrial solutions. An automatic pulse concentration level indicator is the latest development of SKBTsvetmetavtomatika [18].

LITERATURE CITED

1. R. M.-F. Salikhdzhanova and I. E. Bryksin, in: Abstracts of Papers, Fourth All-Union Conference on Polarography, Alma-Ata (1969).
2. R. M.-F. Salikhdzhanova and I. E. Bryksin, Zavod. Lab., 36, No. 3 (1970).
3. R. M.-F. Salikhdzhanova and I. E. Bryksin, Pribory i Sistemy Upravleniya (Regulating Instruments and Systems), No. 9, 41 (1967).
4. B. S. Bruk and B. M. Sternberg, Zavod. Lab., 36, No. 3 (1970).
5. Instruments for Scientific Investigations [in Russian], Collection of advertisements for instruments developed and under development by the institute VNIINauchpribor, Leningrad, Vneshtorgizdat, LO-2804/2165.
6. M. R. Vyaselev, The Method of Oscillopolarography with Stepped Voltage [in Russian], Author's Abstract of a Dissertation, Kazan' (1965).
7. R. Sh. Nagmatullin and M. R. Vyaselev, Zh. Anal. Khim., 19(5) (1964).
8. M. R. Vyaselev, Zh. Anal. Khim., 20 (10) 1048 (1965).
9. A. V. Zheleztsov, Problems of Theory and Instrumentation in ac Polarography [in Russian], Author's Abstract of a Dissertation, Kazan' (1970).
10. A. V. Zheleztsov and M. R. Vyaselev, Zavod. Lab., 34, No. 11, 1289 (1968).
11. A. V. Zheleztsov, Abstracts of Papers, Fourth All-Union Conference on Polarography, Alma-Ata (1969).
12. V. A. Belavin and V. A. Mikhailov, Zavod. Lab., 36, No. 7, 769 (1970).
13. V. V. Senkevich, Zavod. Lab., 36, No. 6, 883 (1970).
14. Yu. A. Ivanov, A. A. Kaplin, and E. G. Trenkle, Elektronnaya Tekhnika, Ser 12, No. 4 (1970).
15. A. I. Miroshnikov, G. G. Gabsalyamov, et al., Zavod. Lab., 33, No. 3, 382 (1967).
16. S. B. Tsfasman and I. E. Bryksin, Zavod. Lab., 28, No. 4, 518 (1962).
17. S. B. Bruk and S. M. Sternberg, Abstracts of Papers, Fourth All-Union Conference on Polarography, Alma-Ata (1969).
18. L. S. Zaretskii, Pulse Polarographic Concentration Level Indicator [in Russian], Energiya (1970).