PROGRESS OF ELECTROANALYTICAL CHEMISTRY
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PART I - FUNDAMENTAL RESEARCHES

Most publications in fundamental electroanalytical chemistry are in the field of polarography, including the use of hanging mercury drop electrodes, oscillographic polarography, a.c. polarography, square-wave polarography absorption phenomena and the study of complex compounds.

In the field of hanging mercury drop electrodes, the problem of experimental verification of the theory of symmetrical spherical diffusion was solved very satisfactorily. Kao *et al.* /1/ used the electrode reaction of anodic oxidation of ascorbic acid to verify the theoretical equation. Experiments were carried out on hanging mercury drop electrodes. The results obtained for limiting currents agreed with theoretical values over a time period of 1200 seconds. Later Kao and Chang /2/ used the reduction of benzoquinone in buffered solution, as the electrode reaction, to verify the general equation at different values of Θ. Kao and Chang /3/ derived a theoretical equation for the diffusion currents of spherical amalgam electrodes in voltammetry at constant potential for the reaction

$$R \xrightleftharpoons{e} O + ne$$

where R represents the metal in the amalgam and O the metallic ion. The instantaneous anodic limiting diffusion current obeys the following equation.

$$i_t = -nFAD_R C_R^* \left(\frac{1}{\sqrt{\pi D_R t}} - \frac{1}{\gamma_0} \right) \qquad (1)$$

where C_R^* is the concentration of metal in the amalgam before oxidation and γ_o the radius of electrode. Experiments with Bi amalgam were carried out to verify the theory. The results agreed with theoretical values satisfactorily. The same equation was obtained later by Stevens and Shain (1966).

From eq. (1), when $i_t = o$,

$$t = \frac{\gamma_o^2}{\pi D_R} = t_o \qquad (2)$$

The plot of i_t against $t^{-\frac{1}{2}}$ gives a straight line, which intercepts the t-axis at t_o, the time at which the anodic current becomes zero. From t_o and γ_o, D_R can be calculated. This leads to a very simple method for the accurate determination of D_R, the diffusion coefficient of a metal in mercury. Using this method, Kao and Chang /4/ determined the diffusion coefficients of 16 metals in mercury and concluded that the diffusion of metals in mercury obeys the Stokes-Einstein equation with n = 4. This conclusion was later confirmed by other investigators.

A series of experiments was carried out by Kao *et al.* /5/ to verify the basic principles of "inverse polarography" suggested by Hickling, Maxwell and Shennan (1956). The results led to conclusions quite different from those of the above workers. In the case of Cd-amalgam electrodes, the diffusion of electroactive metal from the interior to the amalgam-solution interface obeyed the general equation for linear diffusion. Experimental verification of the theoretical equation of Frankenthal and

Shain (1956) was carried out by Chow *et al.* /6/.

Hsu *et al.* /7/ obtained an expression for the evaluation of the diffusion constants of individual complex ions from the measured diffusion current constants. Chang *et al.* /8/ also provided a general treatment for the evaluation of the diffusion coefficients of complex ions from polarographic data.

In the field of single-sweep polarography, Hsu *et al.* /9/ carried out an experimental verification of the Randles-Sevcik equation and pointed out that Sevcik's value of K was too low. Kao *et al.* /10/ carried out experiments on the K 1000 cathode-ray Polarograph to study $i \sim E$ curves with a hanging mercury electrode. The value of the constant obtained agreed with that of Randles. Kao *et al.* /11/ derived a theoretical equation for the current controlled by diffusion and chemical reaction. When $k_f C_z^o = o$ the equation becomes the Sevcik equation for diffusion controlled current. For large values of $k_f C_z^o$ the current is controlled by chemical reaction and a simple equation for catalytic current is obtained. The theoretical conclusions are in good agreement with experimental data for the reduction of Ti(IV)-Oxalate in the presence of $KClO_3$ or NH_2OH. Chang *et al.* /12/ presented a new mathematical treatment for catalytic currents. Hsu *et al.* /13/ studied single-sweep polarography of cadmium ion in the presence of oxygen.

In the field of alternating current polarography, Chen *et al.* /14/ derived equations for catalytic currents and faradic impedance in a.c. polarography. The results obtained agree with those of other investigators. Chang *et al.* /15/ verified the equation for reversible waves in a.c. polarography using the reduction of Ti(IV) oxalate in 0.2 M H_2SO_4 as the electrode reaction. The method described was more rigorous and yielded better results than that reported in the literature. The same authors /16/ verified the theory of catalytic currents. Experimental results obtained were in good agreement with theoretical conclusions for the reduction of Ti(IV) oxalate in the presence of potassium chlorate.

Tsien studied problems relating alternating current and concentration polarization. The non-steady process at the plane electrode was treated /17/, and the faradic impedence of diffusion of spheric and cylindric electrodes was calculated in order to understand the influence of the electrodes /18/.

In the field of square-wave polarography, Chiang /19/ was the first to advocate the so-called "vibrator square wave polarograph", a simple square wave polarograph constructed by attaching two vibrators to an ordinary d.c. polarograph. Chang *et al.* /20/ introduced some innovations in the circuit to render the waves obtained on the "vibrator square-wave polarograph" more stable and reproducible. They derived a theoretical equation for the reversible wave obtained on the vibrator square-wave polarograph and experimentally verified the theory with Cd (II) and Tl(I) ions. /21/ Chang and Kao /22/ also derived an equation for catalytic currents in square-wave polarography, and carried out experiments on a vibrator square wave polarograph to verify their theory /23/. Feng and Liu /24/ constructed a simple robust and high precision mechanical square-wave polarograph which had a very high signal-to-noise ratio. Cd^{2+} and Pb^{2+} ions at concentrations of 2×10^{-8} M could be detected with their instrument. The same authors /25/ derived a theoretical equation for the peak current obtained on their mechanical square-wave polarograph and verified their theory with experiments using Bi (III) and U(VI) ions. Chang *et al.* /26/ derived the equation for a square-wave polarographic current controlled by chemical reaction preceding the electrode reaction. Lee and Yao /27/ discussed the principles for designing a square-wave polarograph and described a detailed circuit diagram of a new type of square wave polarograph /28/.

In the field of a.c. oscillographic polarography, Chiang /29/ discussed the circuit used in the a.c. oscillographic cell on the basis of the Thevenin principle. Kao *et al.* /30/ advocated the use of an internal standard technique in Kalvoda's method. In a procedure for the rapid determination of trace amount of Pb^{2+} in pure hydrochloric acid Ga^{3+} ion was used as an internal standard ion, and h_{Pb}/h_{Ga} was used instead of h_{Pb}. The method gave much higher precision and accuracy than the absolute method. They also used Zn^{2+} as internal standard ion for the determination of Cd^{2+} /31/. Kao *et al.*/32/ used the $dE/dt = f(E)$ curves to indicate the equivalent point of a titration; this method was first advocated by Treindl in 1957. They used EDTA to titrate Ga(III) /32/ and potassium chromate to titrate Pb(II) /32/. The method is much better than ordinary polarographic titration.

Du and Wu /34/ studied the chronopotentiometric reduction of Cd (II) and In (III). The values of $i_0t^{1/2}/c$ obtained at a hanging mercury drop electrode agree with the equation derived by Mamantov and Delahay.

In the field of complex compounds, Hsu *et al.* /35/ obtained a general experession for the evaluation of the successive stability constants of complex ions both in the higher and lower valence states from polarographic data. In four special cases the general expression can be reduced to the results obtained by Lingane (1941), de Ford & Hume (1951) and Jachemirsku (1953). Yen /36/discussed the evaluation of successive stability constants of polynuclear complexes from polarographic data. Hsu /37/ proposed a theoretical expression, similar to the Freundlich absorption isotherm, to express the change of half-wave potentials, oxidation-reduction potentials, solubilities, etc., as a result of complex formation in solution.

Yen and Liu /38/ applied potentiometry with a mercury electrode for the determination of metal chelate stability constants of the EDTA complexes of divalent metals. The log K values found for the Hg, Cu, Pb, Zn, Cd, Mn, Ca, Mg, Sr and Ba-EDTA chelates are in good agreement with those obtained by Schwarzenbach and by Reilley and Schmid who studied the EDTA chelates with the same electrode, but with different experimental procedures. Tsiang and Hsu /39/ determined the half-wave potential of the cadmium ion in sodium perchlorate-sodium thoicyante mixtures and found the existence of Cd $(SCN)_5{}^{3-}$ and $Cd(SCN)_6{}^{4-}$, in addition to the species $Cd(SCN)_4{}^{2-}$, $Cd(SCN)_3{}^{-}$, $Cd(SCN)_2$, $Cd(SCH)^{+}$ and Cd^{2+} found by previous investigators. Hsu and Tsiang /40/ studied the thallous-thiocyanate system with a modified type of H-cell and found evidence for the existence of Tl^{+}, Tl SCN, $Tl(SCN)_2^{-}$, $Tl(SCN)_3$, $Tl(SCH)_4{}^{3-}$ and $Tl(SCN)_6{}^{5-}$ in contrast to the results obtained by others. Tsiang and Hsu /41/ studied the lead and zinc thiocyanate systems polarographically, and found evidence of the existence of Pb^{2+}, $Pb(SCN)^{+}$, $Pb(SCN)_2$, $Pb(SCN)_3^{-}$, $Pb(SCN)_4{}^{2-}$, $Pb(SCN)_5{}^{3-}$, $Pb(SCN)_6{}^{4-}$ in solution. The consecutive stability constants were determined. For the zinc thiocyanate system the experimental data revealed the existence of Zn^{2+}, $Zn(SCN)^{+}$, $Zn(SCN)_2$, $Zn(SCN)_3{}^{-}$, $Zn(SCN)_4{}^{2-}$, $Zn(SCN)_5{}^{3-}$ and $Zn(SCN)_6{}^{4-}$; the corresponding stability constants were calculated. Tsiang and Hsu /42/ studied the zinc thiocyanate system polarographically, and found 6 complex compounds, $Zn(SCN)_x^{2-x}$ with x = 1,2,3,4,5,6. The same authors /43/, /44/ studied complex formation between cadmium and nitrate ions and found evidence for Cd^{2+}, $Cd(NO_3)^{+}$ and $Cd(NO_3)_2$ in solution. The stability constants were found to be $K_1 = 0.62 \pm 0.02$ and $K_2 = 0.16 \pm 0.02$. Pai *et al.* /45/ studied lead nitrate complexes and found $Pb(NO_3)_2$ and $Pb(NO_3)_3^{-}$ in addition to the species reported by others. Kao and Chang /46/ studied the complex ion formed by Pb^{2+} and N_2H_4 polarographically and found the existence of $Pb(N_2H_4)^{2+}$ in solution; the formation constant of the complex is 90 at 30°C. Yen and Ma /47/ used polarographic methods to study the iodide complexes of cadmium. Liu and Fu /48/ studied complexes formed by Cd^{2+} and pyridine and obtained three complex ions. Chang and Liu /49/ studied the cadmium-iodide complexes and revealed the existence of Cd^{2+}, CdI^{+},Cdl$_2$ Cdl$_3^-$, Cdl$_4^{2-}$, Cdl$_5^{3-}$ and Cdl$_6^{4-}$. Pai /50/ studied lead acetate complexes and found four chemical species present in solution: PbAc^{+}, Pb(Ac)$_2$ Pb(Ac)$_3^-$ and Pb(Ac)$_4$. Pai *et al.* /5I/ also studied thallous acetate complexes and found evidence for the existence of Tl(Ac)$_2^-$ in solution in addition to the species reported by others. Chi /52/ studied the polarographic behaviour of uranium in phosphoric acid. Yen *et al.* /53/ determined the formation constants of cadmium halide complexes in perchlorate media. Lo *et al.* /54/ studied the stability constant of copper-tris ethylenediamine.

Wang and Chang /55/ studied the polarographic behaviour of the Sb(III) complex of EDTA. The stability constant and the thermodynamic functions of the Sb-Y complex were calculated. Wang and Shang /56/ studied the polarographic behaviour of Sb(III) with 1,2 diaminocyclohexane-tetraacetic acid (H$_4$Z). The stability constant and the thermodynamic functions of the complex were calculated from the shift of half-wave potential. From the kinetic current, the dissociation velocity constant of the SbZ complex was obtained. Tung and Wang /57/ carried out a polarographic study of acrolein, formaldehyde and acetaldehyde. Wang studied polarographically the substitution reactions between ferricyanide and some ligands /58/ and the decomposition of permanganate in strong basic solutions of complex-forming agents /59/. Wang *et al.*

carried out polarographic studies on Pyrocatechol Violet /60/ and its copper complex /61/.

Gin Du-Man /62/ derived a unified equation for the current-voltage relationship obtained in the polarographic electrode processes of complex compounds, involving currents controlled by rate of diffusion, electron transfer and chemical reaction. Gin *et al.* /63/ studied the polarographic electrode process of the chemical reaction between cupric ion and citric acid and obtained the stability constant of the complex compound. Gin Du-Man /64/ derived a general formula which can be applied to 16 different types of electrode process involving 2 electrons and suggested methods of wave analysis to differentiate various electrode processes. The same author /65, 66/ discussed the relationship between the structure of complex compounds and their electrode processes. The effect of structure on half-wave potential and reversibility of electrode reaction was elucidated. Dong and Wang /67/ discussed methods for identification of various polarographic electrode processes. Gin *et al.* /68/ studied the composition and polarographic behaviour of the Ni(II)-thioglycollic acid complex in solution. Huang and Gin /69/ studied the polarographic behaviour of 2, 6, 7 tri-hydroxyl-9 phenyl fluorone in basic solution (pH 8-14) and obtained a single reversible wave. The same authors /70/ discussed the relationship between polarographic half-wave potential and molecular structure. The application of the Hammett formula and other related formulae in organic polarography was examined.

Tza and Whang /71/ investigated the adsorption of various types of organic surface-active substances in neutral and alkaline solutions by measuring the differential capacity of the dropping mercury electrode. Whang *et al.* /72/ built an experimental apparatus for the measurement of the electrical double-layer capacity of the dropping mercury electrode. Chou and Tza /73/ developed a method using low frequency voltage sweep carrying a measuring signal, for the rapid determination of the differential capacity of the electrical double layer. With this method the whole capacity curve could be seen at once on the screen of an oscilloscope. Tza *et al.* /74/ studied the surface-activity of seven organic complex-forming agents by measuring the differential capacity of the electrode-solution interface. Tza *et al.* /75/ studied the simultaneous adsorption of tetraalkylammonium cations and the β-naphthalene sulphonic acid anion at the electrode/solution interface by measuring the differential capacity of a dropping Hg electrode.

Lo *et al.* /76/ studied the effect of non-ionic surface active substances of the polyethylene oxide type on the hydrogen overvoltage of a mercury electrode. Tian /77/ carried out theoretical analysis of the faradic impedance in cases in which the electrode reaction involves an adsorbed substance. The equivalent circuit for the faradic impedance is obtained for the electrode involving charge-discharge, diffusion and adsorption-desorption processes simultaneously. The effect of an adsorption - desorption process may be expressed by a "compensating impedance" which consists of a resistance and a Warburg impedance in series. Equations for the resistance and the capacitances in the equivalent circuit are obtained. The method for the determination of the kinetic parameters for this type of electrode process was presented. Lin *et al.* /79/ designed a method for determination of the actual area of an electrode through the double layer capacity. Tien /80/ obtained the equivalent circuit of concentration polarization impedance by a "differential method", based on direct comparison of the differential equations formulated for the boundary conditions, diffusion and chemical reactions with those for certain combinations of electric circuit elements. Tien /81/ also discussed the behaviour of autocatalytic electrode processes under constant current on planar and spherical electrodes. The current/time curve of the autocatalytic electrode processes under constant potential on a planar electrode is studied.

Chow *et al.* /82/ studied the electrode process of furfural at the dropping mercury electrode. So *et al.* /83/ also studied the electrode process of furfural at the dropping mercury electrode, using a linearly changing potential and obtained results similar to those of conventional polarography. Lu and Zhang /84/ studied the polarography of sodium tetraphenyl borate and found that Na-TPB gives a kinetic wave at a dropping mercury anode, with the formation of diphenyl mercury.

Hu Yao-Tsun studied the standard electrode and equilibrium potentials of sodium amalgams /85/, potassium amalgams /86/ and zinc amalgams /87/.

Wu *et al.* pointed out that the zero charge potential of antimony may be -0.19 volt./88/ and the value determined in 0.010 M HCl is -0.19 ± 0.02 volt. /89/.

Chang *et al.* studied the electrochemical mechanism of anodic dissolution and self-dissolution of zinc in KOH solutions /90/ and similarly the anodic dissolution of antimony in concentrated solutions of H_2SO_4 and HCl /91/.

Wu *et al.* /92/ studied the anodic oxidation of antimony in sulphuric acid, hydrochloric acid and potassium hydroxide solutions.

Hu and Chow /93/ studied the relationship between "rational electrode potential" and heat of aquation of ions and obtained an accurate method for the determination of the heat of aquation of individual ions. They calculated the numerical values for about forty ions including cations and anions. They /94/ suggested a method for calculation of the absolute values of standard heat of formation of positive and negative ions in water and applied the method to about 150 ions. They also suggested methods for calculation of the heat of aquation of H_3O^+,and calculated /95/ the oxidation-reduction potentials from data obtained in thermodynamics and spectroscopy. Chiang gave methods for calculation of mean ionic activity coefficients from equivalent conductivities of electrolytic solutions /96/ and of individual activity coefficients for uni-univalent electrolytes /97/.

Tza Chuan-Sin /98/ used the polarization surface of a three-dimensional model to interpret electrometric titration processes.

Kao and Hsu /99/ developed a theory for the "dead-stop" titration, which has been verified experimentally for the titration of ceric sulphate with ferrous ion /100/. A series of equations was derived for the intensity of current i as a function of the analytic concentration during titrations from which theoretical titration curves can be obtained.

Chien Jen-Yuan /101/ discussed high-frequency titration curves for various methods of experimental determination (the Q-meter, Z-meter and F-meter methods), using equivalent circuits for C-type and L-type titration cells. The use of Pt wire electrodes in direct contact with the solution was suggested.

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PROGRESS OF ELECTROANALYTICAL CHEMISTRY IN THE PEOPLE'S REPUBLIC OF CHINA (1949 - 1979)

Part II

POLAROGRAPHIC ANALYSIS (NEW TECHNIQUES AND NEW METHODS)

Polarography was developed from the very beginning since the establishment of the People's Republic of China /1-57/ More than 600 polarographic papers have been published including about 40-50 monographs, books and reviews /6-57, 77/. Articles have been selected for this review to provide an overview of progress in the title area such as new polarographic techniques, stripping voltammetry and instrumentation. No particular effort was made to be critical since the range of topics is too broad to permit such a treatment.

Instrumentation

Very early on the CIAC (Changchun Institute of Applied Chemistry, Chinese Academy of Sciences) investigated and produced a classical recording polarograph /58, 59/ which was used by several authors /60-63/. Polarometer, photo- and pen-recording polarographs were produced in Shanghai and Beijing /64,65/. The Shanghai Analytical Instrumental Group produced a photo-recording polarograph /66/ and a pen-recording polarograph type 883 which was sold by thousands /67/. In order to increase the instrumental sensitivity, improve the measuring techniques, make the instrument multifunctional and introduce miniaturisation and automation, some polarographers and corporations in the PRC have investigated and produced various oscillopolarographs /17, 68, 69-78/, a.c. polarographs, square wave polarographs, square wave oscillopolarographs /79 - 91/, pulse polarographs /56, 67, 92 - 96/, etc. In addition, some simple polarographs were produced for universities and laboratories for industrial research and teaching. Polarographs from Amoy Univ. /49, 54, 97, 98/, Fudan University /51, 99, 100/, and the Shandong Ocean Institute incorporated integrated circuitry, in which one piece was used as a linear sweep generator, one or two pieces as a micro-current amplifier or differential amplifier, another as a three electrode system for controlled potential /51, 102/, work etc. This type of polarograph was used with different kinds of solid electrode or TFME (thin film mercury electrode), either in classical polarography or in the differential or stripping mode. Such instruments are simple in structure and cheap,with a rapid scan, etc., both the power consumption and the volume are small. They are light, suitable for pocket use and can be used with an oscilloscope or a recorder. The principle of the 75-3A rapid polarograph is shown in Fig.1. Some home-made polarographs are shown in Table 1.

Oscillopolarography

More than 100 papers on oscillopolarography have been published in China. Some early articles included a.c. oscillopolarography, for the detection and determination of both organic and inorganic substances /17, 27, 68, 103-

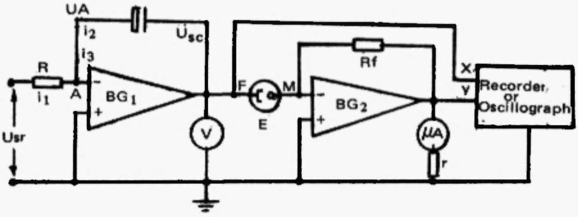

Fig. 1 Diagram of Rapid Polarograph, Type 75-3A

Usr: Input voltage fixed value, R: variable resistance, c: integral condenser, V: voltmeter for applied potential, E: cell, F: reference electrode, M: TFME Rf: resistance selected for sensitivity, μA: microammeter, i: electrolytic current, BG_1, BG_2: linear integrated circuit.

105/, but most articles included current-voltage (I-E) oscillopolarography /45-47, 53, 69-76/. The Chengdu Instrumental Company has produced more than 2000 sets of this instrument which now play a role in several industrial laboratories. For example, in the Hunan Shuikoushan Mineral Centre, more than one hundred thousand data have been reported annually by polarographic methods and more than one hundred kinds of samples are analyzed with only ten oscillopolarographs. In the Chengdu Laboratory Centre No. 715, more than 50 pure metals, ferrous and nonferrous metals, and mixtures are analyzed by oscillopolarography. The quality of these oscillopolarographs is good and any can act not only as normal oscillopolarographs,but also operate in the derivative mode both for catalytic and adsorption waves /49,77/. Some articles describe improvements to oscillo-

Table 1 - Some PRC Polarographs

	Type	Feature	Producer
A. Instrument product	1. Polarograph, 883	Pen-recording classical 3 electrode system, reverse scan and stripping method.	Shanghai Analytical Instruments /67/
	2. Oscillopolarograph, JP-1,JP-1A,SJP-1, SJP-1A, SBJ-2		Chengdu Instruments, Yiyang Radio, Lishui Radio, Jilin Radio /53,53a,76/.
	3. Mechanical Square Wave polarograph,895	Photo-recording	Shanghai Analytical Instruments /80/
	4. Polarograph, AD-1	Rapid scan with HMDE and TFME	Jiangsu Jintan Instruments /51/
	5. Rapid scan polarograph, 75-3A.	With TFME	Amoy 2nd Analytical Instruments /49,54,97,98/
	6. Pulse Polarograph, JP-M1	TFME,electronic-transistor TFME	Jilin F'ct.No. 8270/55, 56,57,95/
	7. Differential Oscillopolarograph, SVA-1	TFME	Shanghai Television Fact. No. 11 /99/.

Table 1 (cont)

	Type	Feature	Producer
B. Laboratory instrument	8. Rapid Scan Anodic Stripping Voltammeter	May also be used as classical with TFME	Fudan Univ. /78,100/.
	9. Pulse Polarograph, F-78	3 electrode system, TFME,transistor-integrated circuit	ditto /96/
	10.Automatic Reverse Polarograph	Automatic continuous sampling determination	Dalian Inst. of Chemical Physics /101/
	11.A.C. Polarograph	Electronic Type and transistor Type.	North Western Univ. and Shanxi Geology Inst. /56, 91/
	12.Square wave polarograph and square wave oscillopolarograph	Electronic	Nankai Univ. CIAC /89, 90/
	13.Oscillator Square Wave Polarograph	Photo- and pen-recording	CIAC, Nanjing Univ. /79, 85/.
	14.Direct Reading Oscillopolarograph	Digital display with reverse scan and differential	Nankai Univ., Jiangsu Metallurgical Inst. /73-75/

Table 1 (cont)

Type	Feature	Producer
15.Multifunction Polarograph	Reverse scan triangular wave, derivative, i-t curve and 1st drop recording	CIAC, Beijing Univ. /71, 72/
16.Pen-recording Square Wave Polarograph	Pen-recording mechanical	Shanghai Boiler Fact. /82/
17.Oscillopolarograph, JPS-5	Base decline compensation	Changzheng Material Fact. /83/
18.Oscillopolarograph, IE-I, IE-II	I-E electronic	CIAC /69, 69a/
19.Rapid Polarograph, JP-H78	Triangular wave, trapezoid wave with programmed controller	Amoy Univ. /84/

polarography. Luo Chang-yin *et al.* /83/ used a curve compensation method to overcome the base declination and thus increased the sensitivity. A differential oscillo-voltammeter manufactured in Fudan University can be used either as a normal oscillopolarograph or in a differential oscillopolarographic stripping mode /99/. A digital reading oscillopolarograph was manufactured in the Jiangs Metallurgical Institute /75/ and Nankai University /74/, which can be used for reverse scan, triangular wave, singl cell (and derivative), double cell differential (and derivative), and digital reading of concentration or content. A rapid polarograph type JP-H78, was manufactured with six integrated operational amplifiers in Amoy University /84/. It included a programmed controller with the function of triangular wave or trapezoid wave and can be used with a 2,3 or 4 electrode system, either as a normal polarograph or for differential or stripping analysis. A multi-function oscillopolaragraph including triangular wave and instantaneous i-t curve device was manufactured in CIAC and Beijing University where the same authors investigated the polarographic electrode process with this instrument /57,71,72/. Basic reasearch on oscillopolarography has been described in various articles /71, 106-108/.

A.C. Polarography and Square Wave Polarography

Research on a.c. polarography including instrumentation has been investigated in Northwestern University /56, 91/. Equations for the a,c. polarographic catalytic current and faradaic rectification have been studied in Nanjing University /109/.

In square wave polarography various kinds of instrument are made in the PRC /79-87/. An oscillator square wave type of polarograph was made in CIAC, Shanghai Metallurgical Institute and Nanjing University. A mechanical square wave polarograph, type 895, designed by the Shanghai Metallurgical Institute was produced by the Shanghai Analytical Instrumental Company and exported to foreign countries. Its sensitivity is quite high and it has been applied in various fields. On the basis of this instrument, some authors from the Shanghai Boiler Factory made a pen-recording polarograph in which they used transistors to generate a slow linear voltage scan and combine it with a mechanical square wave generator,using a high sensitivity galvanometer to measure the polarographic current, but synchronizing the pen of the recorder with a galvanometer light spot. Some square wave polarograms of some cations obtained with this instrument are shown in Fig. 2. Electronic square wave polarographs such as the MKIII made in England, were manufactured in Nankai University, CIAC and the Shanghai Material Institute. A number of papers on the application of square wave polarography have been published by the Shanghai Metallurgical Institute, the Laboratory Centre of Nanjing Geology Bureau and the Beijing Steel and Iron Academy, CIAC /19, 40, 42, 57, 110, 111/. The polarographic process of the square wave polarograph was investigated in CIAC /112/ and equations for the polarographic behaviour of the mechanical square wave polaro-

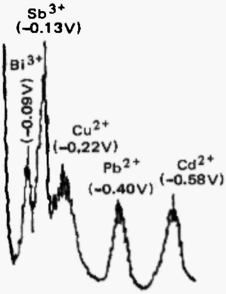

Fig. 2 Square wave Polarogram of 1μg/ml

Bi(III), Sb(III), Cu(II), Pb(II), Cd(II) in IM HCl(82)
10 mV. S=1/3

graph were derived in the Shanghai Metallurgical Institute and Nanjing University /80, 113, 114/.

Pulse Polarography

The pulse polarographic method is the most sensitive method used of all new polarographic techniques. A mechanical pulse polarograph was first built in 1960 in the Shanghai Metallurgical Institute /92/ in which two or three pairs of converters were combined with a classical polarograph to set up a half wave or full wave pulse polarograph. A slowly increasing pulse voltage (25/sec) was applied to the dropping mercury electrode, but the current-voltage curve was recorded only during the last 1/200th sec of each pulse period. An electronic pulse polarograph type, JP-MI, was investigated in CIAC, and then produced in Jilin Factory No. 8270 /56, 67, 95, 116/. It is similar to the Southern-Harwell Model A3100 of

Southern Analytical Limited in the U.K. The integration discharge time (capacitance delay time) and integration gate time (current measurement time) are variable in different sections between 2-40 ms. Cadmium in concentrations down to 1 ppb could be detected. Waves of equal height can be identified when only 25 mv apart. The peak height for the derivative mode is directly proportional to the pulse amplitude. A peak can be detected in the presence of an earlier peak 50,000 times as large when using the drop trigger mode. Satisfactory polarograms are obtained with solutions which have a specific conductivity between that of 5M HCl and 0.01M KCl. In 1977 a seminar on pulse polarography was held in Changchun by CIAC. More than ten papers on basic research and the applications (geology, metallurgy, environmental protection, pure matter, atomic energy, etc.) of pulse polarography were reported /55/. In 1978 a transistor-integrated circuit pulse polarograph, type F-78, was made at Fudan University /96/ involving six integrated operational amplifiers and some transistors. This instrument is light and cheap with a 3 electrode system; its volume is small and its detection concentration is $5x10^{-8}$M. The conductivity of the supporting electrolyte may be less than 0.01M KCl. This instrument is similar to the American polarographic analyzer PAR 174. Both, Types JP-M1 and F-78, pulse polarographs have two modes of operation, normal pulse (or integral pulse) and derivative (or differential). The delay time, scan rate and modulation amplitude of both pulse polarographs are variable over a range. Derivative pulse polarograms for several ions obtained ith the F-78 pulse polarograph are shown in Fig. 3. The ulse polarographic electrode process and stripping methods ave been studied in CIAC /56, 57, 95, 96, 117, 141/.

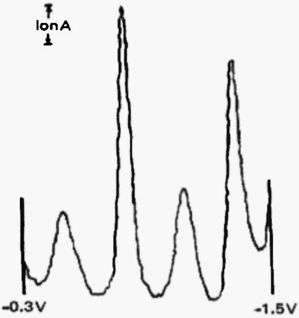

Fig. 3 Derivative Pulse Polarogram of $5x10^{-6}M$ Cu(II), Cd, Ni, and Zn in 1M NH_3-NH_4Cl:2 sec., 2mv/sec., 50mv.

Solid Electrodes and Stripping Voltammetry

Stripping voltammetry using a hanging mercury drop electrode (HMDE) or various solid electrodes or the thin film mercury electrode (TFME) is very valuable for trace analysis /49, 57, 118-153/. The technique can be combined with that of the classical polarograph, oscillopolarograph, square wave polarograph or pulse polarograph elevating the sensitivity by an order of two or three times in the process. Medium exchange is valuable in stripping voltammetry, especially for complex samples where the sample solution is inadequate as a medium for the stripping step, as a result of poor resolution of stripping peaks and interferences resulting from the presence of macro constituents /132/.

Recently, research on solid electrodes has developed rapidly in the PRC; more than 100 papers have been published. There were 46 papers reported in the solid electrode colloquium in Southwest China in 1978. There are various kinds of TFME with different substrates, such as silver wire (or bar) amalgamated with mercury as used in the Qingdao Ocean Institute /49, 151/, a platinum sphere plated by silver and amalgamated in Amoy University /49-57, 97, 144/, a silver sphere coated with mercury in Kunming Metallurgical Institute /49-57, 146-150/ and a glassy carbon (graphite) electrode plated with mercury in CIAC and Fudan University /135-143/. Rough silver wire with a special mercury film treatment has been used in the Shandong Institute of Oceanography /51/ and gold-silver dipped in mercury by the Tianjin Geology Institute /49, 56/. Similarly a wax impregnated graphite electrode has been used in Sichuan University /49/ and a carbon paste electrode in the Beijing Academy of Mineral Metallurgy /49/. A Multiplatinum sphere-thin film mercury electrode combined with a pulse polarograph has been used in the Shanghai Material Institute; the sensitivity is increased by a factor of ten relative to simple TFME, and the results are reproducible /152/. All these electrodes mentioned above are widely used in the PRC. Table 2 shows some examples of the application of the TFME used in Amoy University /49/. Research on some basic problems of these electrodes has been done by others in Nanjing University /122-126/. A study of polarographic and oscillopolarographic behaviour of the HMDE has been carried out in CIAC /120;121/. In order to get reproducible results

Table 2 - Examples of the Application of TFME with a Platinum Sphere Plated with Silver

Example of application	Method	Application Unit
1. Detn.of Cu,Pb,Ni,Zn in minerals.	normal polarographic	Laboratory Centre of the Fujian Geology Bureau, Amoy Univ.
2. Simultaneous detn.of Cu, Pb,Zn,Cd in natural water.	stripping voltammetry	Amoy Univ.
3. Detn.of trace Cu in sea water.	stripping voltammetry	ditto
4. Detn.of trace Zn in sea water.	stripping voltammetry	ditto
5. Detn.of trace Cu,Pb,Zn in pure ZrO_2.	stripping voltammetry	ditto
6. Detn.of Pb,Zn in Cu-alloy.	normal polarographic	Laboratory Centre of the Suzhou Copper Material Plant,Amoy Univ.
7. Detn.of Ni,Zn in copper.	normal polarographic	Amoy Univ.
8. Simultaneous detn. of Bi, Cd,Pb in Al-alloy	normal polarographic	Chem.Laboratory, Yongan Machinery Fact. in Fujian
9. Detn.of Bi,Cd in Zn-alloy.	normal polarographic	Amoy Univ.
10.Detn.of Pb in alloy steel.	normal polarographic	ditto
11.Detn.of trace metals in water.	stripping voltammetry	ditto

Table 2 (cont)

Example	Method	Application Unit
12.Rapid detn. of Cu in Al-alloy.	normal polarographic	Chem.Laboratory, Fact. No. 313 in Fujian
13.Rapid detn.of Zn in Al-alloy.	normal polarographic	ditto
14.Detn.of trace Pb in copper.	stripping voltammetry	Laboratory Centre, Suzhou Copper Material Plant
15.Detn.of Cu,Zn in Al-alloy.	normal polarographic	Laboratory Centre, Huachuan Machinery Fact.
16.Detn. of Zn in Al-alloy.	normal polarographic	Laboratory Centre, Nanping Electric Machinery Fact.
17.Detn.of small amount of Ni in Cu-alloy.	normal polarographic	Laboratory Centre, Suzhou Copper Material Plant
18.Simultaneous detn.of Cu,Ni,Zn in Al-alloys.	normal polarographic	Laboratory Centre, Neimenggu 1st Machinery
19.Detn.of Cu,Ni in steel.	normal polarographic	ditto
20.Detn.of formaldehyde.	normal polarographic	Polarographic Laboratory, Heilongjiang Institute of Environmental Protection

it is very important to make the solid electrode and TFME fresh and not to have it contaminated by adsorption or inactivated by passivation. The treatment of the electrode surface plays an important role and it is necessary to study further details although many papers on this issue have been published already. Some authors from the Qingdao Ocean Institute used alginic acid or its calcium salt as an electrode anti-adsorption membrane /51/ thus providing the possibility of solving the adsorption problem on solid electrodes. Work on organic analysis with solid electrodes has been done in the Heilongjiang Environmental Protection Institute /153/. Mao Xin-chun used the pilot method to determine impurities in pure aluminium /152a/.

Miscellaneous

The development of polarographic analyzers is an active area of research in the PRC. Many different kinds of polarographic analyzer have been constructed and combined with ion exchange methods, etc., and special instruments for uranium, oxygen, sulphur dioxide,etc., have been made. /56,154-156/. Polarometric and oscillopolarometric titrimetry can increase the precision of the polarographic method and have been used in laboratories in industry /157-163/. There were also many papers on organic polarography /104, 105, 153, 164-171/.

In a word, polarographic analysis has developed considerably in the PRC during the past 30 years. It will **un**doubtedly be developed further as a result of the modernization of China's industrial and scientific capabilities.

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PROGRESS OF ELECTROANALYTICAL CHEMISTRY
IN THE PEOPLE'S REPUBLIC OF CHINA
(1949 - 1979)

Part III

POLAROGRAPHIC CATALYTIC WAVES

In modern analytical chemistry, there is a continuous need to find sensitive and selective analytical methods. The use of polarographic catalytic waves which have their theoretical basis in electrochemistry and chemical kinetics provides an effective means of enhancing the sensitivity and selectivety of polarographic analysis.

As early as 1932, the catalytic waves of some organic substances, the Co-protein system and some of the platinum group metals were reported in the literature. Since then, more than one thousand papers have discussed the mechanism (also some applications) of the famous Brdicka catalytic wave, but without satisfactory conclusion. Much attention has been paid to theoretical investigations,but there have been relatively few applications to trace analysis.

During the past thirty years,more than 40 new catalytic polarographic waves of about 30 elements have been proposed by analytical chemists in industrial laboratories, colleges and institutes in the PRC. The mechanism of some of these catalytic waves have been carefully studied, but most of them have been applied to trace analysis of high-purity materials, metallurgical products, minerals, complex ores and environmental monitoring with satisfactory results. For example, the catalytic waves of Mo.Co.Rh.Ir.Se, etc., have such high sensitivity that their limits of detection are as low as 10^{-9} to 10^{-11}M with very few interferences. The apparatus used to obtain these catalytic waves were ordinary D.C. polarographs or cathode-ray polarographs made in China and since these are available in most analytical laboratories, they offer the possibility of methods that are rather simple, rapid, sensitive, and accurate.

Here we summarize the experimental conditions and the applications of some of the most important catalytic waves studied in China.

Ti and V.

The polarogram of Ti(IV) in $H_2C_2O_4$-NH_2OH or $KClO_3$ solution shows a typical parallel catalytic wave /1/. The rate constant k_f for the parallel chemical reactions in $KClO_3$ solution has also been determined by polarography with linearly changing potential /2/. The method has been used to determine trace amount of Ti in pure silicon with a sensitivity of 1×10^{-6}M /1/.

Several catalytic systems have been proposed for vanadium. In the V(v)-Na(K)H_2PO_4-H_2O_2 system, a catalytic wave is obtained as shown in Fig. 1 /3/ due to the adsorption of the catalytically active complex on the dropping mercury electrode. The mechanism of this catalytic wave has been elucidated and the composition and stability constant of the active vanadium complex was determined by

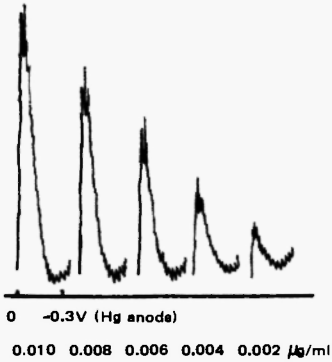

Fig. 1 Catalytic wave, 891 polarograph
$V(v)-K(Na)H_2PO_4-H_2O_2$

measuring the catalytic current. The method may be applied to determine V in optical fibers as low as $0.1 ngcm^{-3}$ /4/.

The catalytic wave of the V(v)-mandelic acid-$NaClO_3$ system has also been studied. Under suitable conditions the peak current is linearly dependent on concentration over the range 10^{-7} to 10^{-8}M and may be applied to ore analysis /5/. V(v) can catalytically decompose mandelic acid (by heating) to benzaldehyde which is then polarographically determined, thus providing an indirect method for the determination of V in minerals and rocks, such as chromite containing 0.x% to 0.000x% V_2O_5 /6/, and also for the analysis of traces of vanadium in coals /7/.

Nb and Ta

The polarogram of a weak acidic solution of Nb(V) and

Ta(V) in the presence of a small amount of EDTA and $PtCl_4$ shows two catalytic waves as in Fig. 2 /8/. The sensitivity of the Nb wave is $3x\text{-}10^{-7}$M and that of Ta is $5x10^{-6}$M. At pH-4.4, the presence of Ta in amounts hundred times greater than Nb does not interfere with the determination of Nb. A different kind of mechanism for the catalytic wave has been suggested in order to explain the peak potentials being more positive than the $E_{1/2}$ of the waves of their EDTA complexes in the absence of $PtCl_4$.

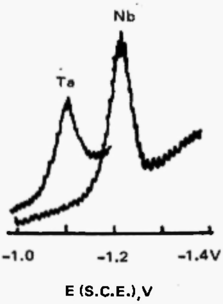

Fig. 2 Catalytic Waves
Nb(v)-Ta(v)-EDTA-$PtCl_4$

Nb(V)-mandelic acid-$NaClO_3$ solution in the presence of small amounts of $(CH_3)_4NBr$ gives a catalytic wave of sensitivity $1x10^{-9}$ /9/. It has been applied to the analysis of Nb ores.

Cr, Mo and W

The polarogram of Cr(VI, III) -α-α dipridyl-$NaNO_2$ in an ammonical buffer solution shows a sensitive catalytic wave

(E_p=-1.45 v SCE), the lower limit of detection of which is $1x10^{-10}$M/9/, while in a solution of ethylenediamine and $NaNO_2$ a catalytic wave (E_p=-1.47v SCE) appears with a sensitivity of $1x10^{-9}$M/10/. The function of NO_2^- in the catalytic wave has been discussed. The method was used to determine the Cr(VI) and Cr(III) contents of tap water without any preconcentration.

The catalytic wave of the Cr(VI)-NH_4Cl cupferron system is also sensitive enough to determine 0.002-0.06 μg/ml Cr(VI.III) in ores /11/. It is more sensitive than either colorimetric or atomic-absorption spectroscopy by two orders of magnitude.

In 1963 Deng Jie-Qu(Fudan University) first suggested a very sensitive ($6x10^{-10}$M) catalytic wave for Mo(VI) with E_p=-0.5 v(SCE), which used mandelic acid as a complexing ligand. /12/ It is more sensitive by two orders of magnitude than a similar catalytic wave of Mo(VI) reported by ПАХОМОВА *et al*, in 1976 /58/. It has been used to determine trace amount of Mo in natural waters /13/, ores /14/, steels /15/, soils /16/ and cereals /17/. Mo(VI) in other α-hydroxycarboxylic acids also shows catalytic waves which are suitable for analytical purposes /18/. Mo(VI) reacts with phosphoric acid or arsenic acid to form poly-acids which may be used as an indirect method to determine P in semi-conductor materials or as in natural water /57, 13/.

The polarogram of W(VI)-HCl-KCl exhibits a catalytic peak (E_p=-1.3 v SCE) which can be used to determine 10^{-7}-10^{-6}M W. This wave is probably a catalytic hydrogen wave. W(VI) has a catalytic wave in H_2SO_4-mandelic acid $KClO_3$ system which is similar to that of Mo(VI). With the addition of small amounts of cinchonine, W(VI) can be detected as low as 0.000x% W in ores without preconcentration /19/. The method is more sensitive by two orders of magnitude than the W(VI)-$H_2C_2O_4$-H_2O_2 system ($5x10^{-6}M$) reported by Oshea *et al*, in 1972 /59/.

Mn and Re

The polarogram of the Mn(II)-TEA-NaOH-KIO_4 system shows a catalytic wave of $1x10^{-5}M$ sensitivity /20/; the stability constant of $Mn(TEA)_2^{2+}$ has been determined to be $K=4x10^7$.

The derivative polarogram of Re(VII)-H_2SO_4-NH_2OH-ascorbic acid in the presence of traces of TeO_3^{2-} shows a catalytic wave with a sensitivity of $2x10^{-7}M$ /21/: With the addition of a suitable amount of benzaldehyde, the lower limit of detection is $2x10^{-8}M$ /22/. A procedure has been proposed for the determination of Re in ores and in control analysis for metallurgy. The mechanism of this complex system has been studied.

Co and Ni

Much research work has been done on the catalytic waves of Co and Ni both in China and other countries. The mechanism and behaviour of the catalytic waves of Co and Ni have been fully studied in many countries, while in China, several sensitive catalytic systems were proposed for the determination of trace amounts of Co and Ni. The catalytic waves are formed through the adsorption on mercury of the Co or Ni complexes of organic ligands containing $-NH_2$ or -SH radicals thus lowering the overpotential of hydrogen evolution, so that they yield catalytic hydrogen waves.

Catalytic hydrogen waves are the most important types of polarographic catalytic waves. The catalytic waves of the Pt group belong to this kind. Their mechanisms are not very clear, however, because the electrode processes are complicated by the phenomena of adsorption.

Somewhat less sensitive catalytic waves of Co and Ni have been found in $KSCN-HNO_3-HNO_2$ solutions /23/. Those used in metallurgical and geological analysis are as follows:

1. Co(II)-pyridine-dimethylglyoxime-NH_4Cl system /24/. In the cathode-ray polarograph, JP-1A, the limit of detection is 0.001 μg/ml.

2. The catalytic current of the cathode ray polarogram of the Co(II)-dimethylglyoxime-$NaNO_2$-NH_4Cl(pH 7-8) system (E_p=-1.20 v,SCE)is two thousand times larger than the diffusion current and is linearly dependent on concentration in the range 10^{-8}-10^{-10}M /25/. About 0.1 g of ore sample is enough for analyzing Co and Ni. Ni also exhibits catalytic waves under similar conditions, but they are less pronounced. Fig. 3 shows the normal and derivative cathode ray polarograms of Co(II) and Ni(II).

3. The catalytic current of the polarogram of Co(II)-NaOH-α,α-dipridyl-NH_2OH system is ten thousand times larger than the diffusion current in ordinary ammoniacal

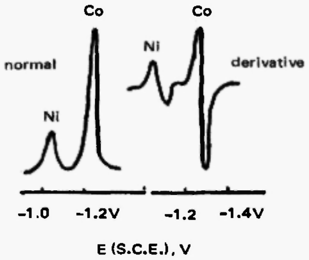

Fig. 3 Catalytic Waves, JP-1A
Ni(II)-Co(II)-dimethylglyoxime-$NaNO_2$

solution. The limit of detection is $1x10^{-9}M$ /26/. More than 20 foreign ions at certain concentrations were tested and gave no interference.

4. Co(II)-dimethylglyoxime-ammonium citrate-NH_2OH system. This has a sensitivity of 0.003 μg/ml /27/. The addition of hydroxylamine improves the wave form and eliminates the interferences of Fe^{3+} and V^{5+} by reducing them to a lower valency. By increasing the amount of NH_2OH, the method may be applied to determine trace amounts of Co as low as 0.0002 μg/ml in water.

5. Co(II)-dimethylglyoxime-NH_2OH(pH=9) system. This system has a sensitivity of $1.6x10^{-8}M$ in D,C. and $1x10^{-9}M$ in cathode ray polarography (E_p=-1.02 v, Ag-Hg anode)/28/. The addition of a small amount of gelatin can stabilize the wave and the method may be used in the analysis of Co in rocks and minerals.

6. Ni-H_2SO_4-KSCN-$NaNO_2$ system. This has a sensitivity of 0.000x% when trace amounts of As(III) are present /29/.

It may be used in the analysis of Ni in iron ores and steels /29, 30/.

Furthermore, Co and Ni may be determined simultaneously under suitable conditions. For example, system (4) has been used to determine Co and Ni simultaneously in rocks. The method is now used in routine analysis.

7, The polarogram of Ni-α,α'dipyridyl-$NaNO_2$-EDTA in ammonical solution shows a catalytic wave with a sensitivity of 0.01 μg/ml for Ni. It is probably an induced catalytic hydrogen wave due to the adsorption of the mixed ligand complex $Ni(C_{10}H_8N_2)_2(NO_2)_2$ on the electrode surface /31/. If Co(II) is also present there are two wave peaks as shown in Fig. 4.

8. Ni- dimethylglyoxime-$(CH_2)_6N_4$-NH_4Cl system. The catalytic wave in this system is sensitive and selective /32/ and is now used as a standard method for the determination of Ni in manganese ores.

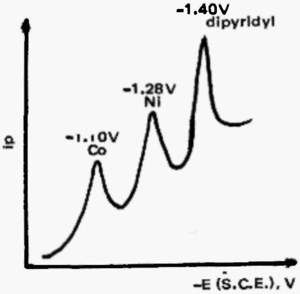

Fig. 4 Catalytic Waves
Ni(II)-Co(II)-α,α'dipyridyl-$NaNO_2$-EDTA

Metals of the Pt Group

The catalytic waves of the Pt-group have been described in detail in the monograph: "The Polarographic Catalytic Waves of the Platinum Group Metals" /33/. Some examples reported since 1974 are given here.

1. Pt(IV)-H_2SO_4-NH_4Cl-$(CH_2)_6N_4$ system. The sensitivity of the wave is 0.00005 μg/ml ($2.5x10^{-10}$M) corresponding to 0.0000xg/ton in ores /34/. It is much more sensitive than the catalytic wave (0.003 ppm.) reported by Alexander *et al,* 1977 /60/ by pulse polarography.

2. Ir(IV)-HCl-thiourea-KI in presence of a small amount of $TeO_3^{=}$. The limit of detection is as low as 10^{-5}-10^{-3} mg/ml ($5x10^{-11}$-$5x10^{-9}$M). Both the extremely sensitive waves of Pt and Ir are used in the routine analysis of ores /35/.

3. Pd(II) has no catalytic wave, probably due to the formation of an intermetallic compound. Recently a catalytic wave in Pd(II)-0.1 M NaOH-$1x10^{-3}$M 1,2 cyclohexanediketonedioxime was found in derivative cathode ray polarography (E_p=-1.02 v, SCE) /36/. Although the structure of the complex may be similar to that of Co(II) or Ni with dimethylglyoxime, the wave cannot be supposed to be a catalytic hydrogen wave in a strong basic solution. We suggest that such a wave should be called a complex-adsorptive wave. In cathode ray polarography the concentration of Pd(II) in the range $5x10^{-8}$-$5x10^{-5}$M bears a linear relationship with the catalytic peak currents. The method is used in ore analysis.

Cu, Cd, Pb and Sn

In H_2SO_4-KSCN-NH_2OH medium, Cu(II) gives a maximum-like peak (E_p=-0.45 v,SCE), which is used as a standard method for the analysis of copper in manganese ores /37/.

The derivative cathode ray polarograms of Cd^{2+} and Pb^{2+} in KI, KSCN or KBr medium show adsorptive catalytic waves which may be utilized to determine Pb^{2+} and Cd^{2+} in concentrations as low as 5 μg/l /38/. Pb^{2+} and Cd^{2+} may be determined simultaneously in the presence of KI. This method is very useful in water pollution analysis.

In the system Sn(IV,II)-HCl-NH_4Cl-V(IV) we observed a good catalytic wave (E_p=-0.5 v, SCE) in which the role of V(IV) was investigated. The method has been applied to the determination of microgram quantities of tin (10^{-8}-10^{-6}M) in various materials such as pure metals, alloys, electrolytic copper, lead-base alloys, rare earth cast irons, etc. /40/. When the composition of the medium is changed to H_2SO_4 and NaCl instead of HCl and NH_4Cl, the method can be applied to ore analysis for 0.005-0.5% Sn: Pb^{2+} does not interfere /41/.

NO_2^-

An anionic catalytic wave of NO_2^- was found in V(IV)-HCl solution and may be used for the determination of NO_2^- in the concentration range 5×10^{-5}M to 1×10^{-3}M /42/.

As, Sb and Bi

The polarograms of As(III) and Sb(III) in Na_2SO_4-$CoSO_4$

solution exhibit catalytic waves with a sensitivity between 10^{-7}M and 10^{-6}M /43/. With the aid of radioactive tracers ^{60}Co and ^{124}Sb to study the composition of the Sb complex, the waves were identified to be catalytic hydrogen waves.

The polarogram of As(III) in H_2SO_4-NH_4I-TeO_3^{2-}-(C_2H_5OH)-gelatine exhibits an adsorptive catalytic wave (E_p=-0.6 v, SCE), which may be used to determine trace amounts of As in antimony ore, tin ore, water pollution analysis, and, in human hair, as an early diagnosis of cancer. The limit of detection is 1×10^{-9}g As/ml, when a cathode ray polarograph is used.

The cathode ray polarogram of Bi(III) in the NaOH-mannitol-pyridine-PAR system shows a sharp adsorptive peak, the detection limit of which is 0.001 µg Bi/ml in ore analysis /44/.

Se and Te

Using a multifunctional cathode ray polarograph, self-designed and installed in our laboratory, we investigated the polarographic behaviour of Se(IV) and Te(IV) in basic Na_2SO_3 solution /45/. It was shown that the Se(IV) peak is due to the reduction of HgSe formed at the electrode surface. The limit of detection of this peak is 5×10^{-7}M Se. The maximum on the second reduction wave of $TeSO_3^{2-}$ was identified to be due to the adsorption of Te(0), without the liberation of H_2. The limit of detection of this peak is 5×10^{-8}M Te.

1. The very sensitive peak of Se(IV) in the Na_2SO_3-EDTA-

NH_4CI-KIO_4 gelatine system may be used to determine 10^{-6}%-10^{-4}% Se in ores /46/.

2. The peak current at -0.85 v,SCE of the polarogram of Se(IV) in a o-diphenylamine system in the presence of Ga(III) may be used to determine 0.005 μg/ml of Se /47/.

3. The peak of the polarogram of the Te(IV)-H_2SO_4-NaCl system in the presence of Cu^{2+} has been used to analyse Te in ores as low as $3.2x10^{-8}$M /48/. The mechanism of the "maximum" on the second wave of the polarogram of Te(IV) in H_2SO_4-$KCIO_3$ was investigated /49/.

4. When Te(IV) and Re(VII) were present together in a solution containing some polyethylene alcohol under optimum conditions, Te could be detected down to $6.5x10^{-10}$M /50/. It is probably an adsorptive and parallel catalytic wave.

Rare Earths

The catalytic waves of the rare earths have not been reported in the literature. Recently some catalytic waves of rare earths have been investigated in China.

1. The polarogram of Yb(III) in NH_4Cl-KNO_3 or $NaNO_2$ shows a catalytic wave at $E_{1/2}$=-1.47 v, SCE /51/. With the addition of tetraammonium salts and polyethylenealcohol, the catalytic wave has been used to determine 10^{-7} to 10^{-6}M Yb in ores. Other rare earths do not interfere under certain limits of concentration. This mechanism is being studied further.

2. A complex-adsorptive wave has been observed in the derivative cathode ray polarogram of Sc(III) in the NH_4Cl -cupferron-diphenylguanidine system which has a sensitivity of $5x10^{-8}M$ Sc /52/. The derivative peak is sharp and nearly symmetrical and may be used in ore analysis with no interference from other rare earths after a simple extraction.

3. The polarograms of Y and all lanthanides except Eu and Pm (which has not been tested) in the NH_4Cl (pH 4-5)-cupferron or rhodamine B system show sensitive adsorptive catalytic waves /53/. The peak potentials of the cupferron system are all near -1.6 v, SCE. The lower limits of detection for Nd^{3+} and Tb^{3+}, for example, are about $5x10^{-8}M$ /53/. That Eu^{3+} shows no catalytic wave in the above-mentioned conditions is probably due to its easy reduction to Eu^{2+}. If a sample of mixed rare earths is to be analyzed, it is recommended to separate them by liquid chromatography and then to determine the contents of the individual rare earths polarographically.

Actinides

A catalytic wave in U(VI)-H_2SO_4-V(IV) solution has been obtained, in which the catalytic current is 20 times higher than the diffusion current without V(IV) /54/.

We investigated the dismutation reaction of U(V) in different organic and inorganic acids and measured the rate of auto-catalysis in the presence of different anions /55/. On the basis of these studies, two catalytic polarographic systems have been proposed, the

U(VI)-citric acid-V(IV) system and the U(VI)-KSCN-H_2O_2 system /55/. The catalytic wave in another system, U(VI)-HAc-NaAc- cupferron, is even more sensitive and may be used to determine from $1x10^{-8}M$ to $8.5x10^{-6}M$ uranium in ores containing some W and Mo /56/.

A little work has been done in the PRC on organic catalytic waves. However, some medical research centers apply the method of the Co cysteine catalytic waves as a diagnosis of cancer with success. They also study the polarographic behaviour of putremine, spermidine and spermine in the presence of trace amount of Cu^{2+} as a catalyst, the method seems to be promising for the early diagnosis of cancer.

From the above review, it can be seen that polarographic catalytic waves provide one of the most sensitive analytical methods for the determination of trace amounts of many elements. Further studies both on the theoretical and applied fields of polarographic catalytic waves are being carried on with considerable enthusiasm.

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PROGRESS OF ELECTROANALYTICAL CHEMISTRY IN THE PEOPLE'S REPUBLIC OF CHINA (1949 - 1979)

Part IV

ION SELECTIVE ELECTRODES

During the past twenty years, ion selective electrodes appear to have been one of the most active research areas in the development of analytical chemistry. The technique involving only a measurement of ion activity or concentration with an ion selective electrode is rapid, accurate and economic as well as suitable for the automation of routine analysis. The earliest available ion selective electrode is the H^+ responsive glass electrode, but since the sixties many other classes of electrode have been developed. In the PRC, analytical chemists and workers have been active in this field. Many technical seminars have been held for the exchange of information, making comprehensive comments, translating foreign articles, etc. This paper aims at giving a brief review according to the development and classification of electrodes as follows.

Glass Electrodes

pH glass electrodes are the earliest selective electrodes for hydrogen ions. There were no normal commercial products available in the PRC till after liberation. At that time, while instrumental analysis was being developed, there were many papers dealing with the preparation and repair of electrodes.

The first Chinese glass electrode for alkali metal ions was the sodium electrode designed by Shu Yu-sun /1/; the range for sodium was 10^{-1} - 10^{-4}M. An investigation of the transformation principle on 85 kinds of Na-Al(B)-Si glass was carried out by Wuan Er-li *et al* /2/, and K-325 was selected as the potassium functional glass. Several workers at the Nanking Institute of Soil Science /3/ studied sodium functional glass for its capability to withstand interference from hydrogen ions.

Solid-state Crystal and Heterogeneous Membrane Electrodes

After glass electrodes, halide ion selective electrodes were developed. The first attempt to make the solid-state lanthanum fluoride electrode was made by the Shanghai Institute of Metallurgy /4,5/. Other institutes such as Hunan University /6/ have studied the factors affecting the potential including the temperature and the time taken for final equillibrium. Single crystals of LaF_3 and commercially available electrodes have been manufactured later by the Changsha Semiconductor Materials Factory. After improvement, year by year, an all solid-state LaF_3 crystal electrode doped with calcium fluoride has recently been produced. This quite excellent electrode has a limit of detection down to $2x10^{-7}$ M F . The fluoride ion electrode has been applied extensively in China, e.g. for the determination of fluorine in rocks and minerals /7/, in calcium phosphate /8/

and slags /9/; the indirect determination of aluminium /10/ and rare earths /11/ in steel and alloys and fluoride in black chrome plating bath solution and waters /12/. Chang Kuo-hsing, *et al*,/13/ suggested the optimum method of masking aluminium with Tiron in the analysis of alumina. The electrodes have also been applied to the analysis of cement and its raw materials /14/. In the analysis of ethyl orthosilicate, based on the principles of precipitation of K_2SiF_6 in 2 M HNO_3 solution in the presence of excess potassium salts, analysts in the Shanghai Institute of Metallurgy /15/ added excess amounts of fluoride and then measured the remainder with the fluoride electrode so to determine silicon indirectly. The experiments also verified that electrodes treated with 2 M acid still exhibit a linear response to fluoride ion. In the Shanghai Research Institute of Labour Health and Occupational Diseases Prevention, analysts using the electrode detected fluoride in urea, blood, organs of animals, water and air. Using the electrode, Wang Chang-yi and Li Yi-chun /17/ improved the original operation of analysing bones. Liu Kai-xiang and his co-workers /18/ used the electrode as an indicator to detect fluoride in the automatic titration of lanthanum nitrate. Environmental analyses were also carried out in the Yunan Research Institute of Chemical Engineering /19/ with the electrode. In addition, there are many reports on analytical applications of fluoride ion selective electrodes and Liu Kai-xiang /20/ has summarized them comprehensively.

So far as solid-state electrodes for Br^-, Cl^- are concerned, disk type commercial electrodes based on pressed disks of Ag $\cdot Ag_2S$ were designed by Yu Rui-bao *et al,*/21, 22/. Bromide ion-selective electrodes were used for detecting bromine in colored glass made by the Shanghai Institute of Silicates /23/. A high sensitivity chloride ion selective electrode was made by Fudan University /24/ with $HgCl_2$ as the electroactive component; its linear range extends from 10^{-1} - 10^{-6} M. The chloride ion selective electrode has been used to measure chloride ion concentrations in copper-zinc electrolyte /25/, water /26/ and ores /27/.

As for iodide ion selective electrodes, Zhu Chong-yi /28/ made a comparison between a AgI-paraffin membrane electrode and a pressed disk electrode for determining I^- in seaweed. Wang Chang-yi /29/ used the same electrode for the analysis of organic compounds. A pressed disk iodide electrode of 95% AgI-5% Ag_2S was made and applied by the Chinghai Institute of Salt Lake Research /30/. Zhu Peng-ling /31/ designed an all solid-state AgI-Ag_2S electrode. The Shenyan Institute of Forest and Soil Science /32/ used a pressed disk AgI electrode for the determination of CN^- in sewage. The Yunnan Institute of Chemical Engineering /33/ found the lower limit for the electrode to approach 0.026 ppm CN^- in the analysis of water, wine and air. Kirin University /34/ used the electrode for the analysis of electroplating bath liquor and Han Wei and Li Shi-jio /35/ suggested the assay of mercury in minerals by determinging residual iodide with the ion selective electorde. Several workers also made applications to the detection of sulphur in steels using the electrode as an indicator for the indirect determination of reduced I_2 after combustion /36/ and for the determination of iodine in phosphorus ores /37/. The detection of mercury in sewage using an ion selective electrode made with Ag_2HgI_4 has been described by Dai Wen-feng *et al*, /38/.

The first Ag_2S pressed disk electrode in China was prepared by Hunan University /39/. Tsou Ai-min and his colleagues /40/ compared methods for the precipitation of Ag_2S and the preparation of different types of electrode and used them for the determination of trace amounts of silver in pure lead. Mo Mao-sheng and He You-zhen /41/ used an Ag electrode for the analysis of Ag in ore, within the range $10^{-2} \sim 10^{-7}$ M. Feng Da-min /42/ proposed an indirect method for the determination of phosphorus in Ni-Ti alloys.

Han Ying-min and Yu Rui-bao /43/ prepared a copper ion selective electrode from a pressed CuS-Ag_2S disk. The Canton Institute of Testing and Analysis /44/ applied the electrode to the detection of Cu^{2+} and SO_4^{2-} in copper-plating liquor.

Wu Fen /45/ introduced an all solid-state lead ion selective electrode with a mixed precipitate of 30% PbS-70% Ag_2S without $PbSO_4$. This electrode is sensitive to $1x10^{-7}$ M Pb^{2+}, and has a long lifetime, and obvious potential breakthrough during the titration of SO_4^{2-} in 25% alcohol. Yang Xiu-rong and Pu Guo-gang /46/ reported the determination of lead in soils using a pressed PbS-Ag_2S sintered disk electrode.

A CdTe-Ag_2S ceramic membrane electrode had been made by the China National Institute of Metrology /47/ and using this electrode quantities of cadmium in natural waters and sewage sludge were detected. Kuang Ping-xian *et al,* /48/ used self-made CuTe-Ag_2S electrode to detect copper in minerals and soils.

Electrodes with Mobile Carrier

Electrodes known as liquid ion-exchanger membrane electrodes, liquid membrane electrodes and neutral carrier electrodes are now called "mobile carrier electrodes". These can be categorized as: positively charged, negatively charged and uncharged carriers. All these electrodes have been developed and reported in the PRC. The Nanking Institute of Soil Science /49/ first made a nitrate liquid membrane electrode responding to NO_3^- in the range of 10^{-1} ~ 10^{-5} M. Wu Fen /50/ prepared a similar electrode using a quarternary ammonium salt "7402" as ion exchanger and o-nitrophenyldodecyl ether as diluent to detect NO_3^- in sewage and natural water. Based on long linked quaternary ammonium bromide as active component and dioctyl-p-phthalate as plasticizer. Lu Wen-ying *et al,* /51/ proposed a PVC membrane nitrate ion electrode with a limit of detection as low as 1×10^{-6} M NO_3^{2-}.

Liu Yan-ming *et al,* /52/ prepared a ClO_4^- electrode based on Crystal Violet-ClO_4^- complex compounds. It's linear response is over the range 10^{1} ~ 10^{5} M ClO_4^-. The performance of electrodes based on Brilliant Green-ClO_4^- -chlorobenzene with a PVC-tetranydrofuran jelly as inert support was better than similar electrodes from abroad. Niu Dei-sheng *et al,* /53/ prepared a mobile carrier electrode based on a Crystal Violet-$Zn(SCN)_4^{2-}$ emulsive film on PVC as an inert support material. This responded to both SCN^- and $Zn(SCN)_4^{2-}$ and they claimed that emulsive film electrodes have some advantage over PVC but a smaller linear response range. In addition, there is a Brilliant Green - $Zn(SCN)_4^{2-}$ - PVC electrode.

Chang Kuo-hsing and his colleagues /54/ tested four systems of quarternary ammonium - BF_4 - PVC electrodes and suggested that electrodes with 2% triheptyldodecylammonium iodide, di-(2-ethylhexy) benzoate 30% PVC as electroactive component were the best over the range 10^{-1} to $3x10^{-6}$ M BF_4^-. This electrode behaves in a completely Nernstian manner and has a low limit of detection, down to $9x10^{-7}$ M. As to the selectivity coefficient for other ions, it is better than present commercial electrodes and can be used to measure boron directly in the transformed form of HBF_4.

A calcium ion PVC membrane selective electrode made by the Suchow Measures and Standards Office based on di-(2-iso-octylphenyl) calcium dihydrogen phosphate as active material is commercially available and its limit of detection is as low as 10^{-5} M Ca^{2+}. Chang Tsu-hsuan *et al,* /55/ used a calcium ion electrode for the study of the normal free calcium in brain samples of mice. They concluded that compared with various other methods of determination such as complex titration and atomic absorption, the calcium ion electrode method is more reliable, although the analyses obtained are somewhat lower.

A potassium concentration of 1x10^{-6} M can be detected using the 4,4'-di-tertiary butyl dibenzo-30-crown-10 potassium ion selective electrode developed by the Lanchow Institute of Chemical Physics /56/. Huang De-pei /57/ fabricated barium ion selective electrodes using the non-ionic surfactant, pelargonic benzoxypolyethylene oxide-ethanol as neutral carrier. Its linear range is 10^{-1} to 10^{-5} M Ba^{2+}.

Gas-sensing probes

A new achievement in the field of theoretical studies has resulted in an electrode which acts as a gas-sensing probe and incorporates an electrochemical sensor and a gas-diffusion membrane. The ammonia gas sensing probe made by the Shanghai Institute of Metallurgy /58,59/ has been applied to the determination of nitrogen in steel /60, 61/. It was also used by Hunan University /62/for the determination of ammonia in sewage and air. Li Ru-bai *et al,* /63/ reported the use of the ammonia gas-sensing electrode for the analysis of coal and soils.

Cyanogen /64/ and sulphur dioxide sensing probes./65/ have been tested by Hunan University. Yiu Shiu-jian and her colleagues /66/ made a carbon dioxide probe and applied it to the determination of free CO_2 in water.

Others

The standard addition technique has been applied in analysis with ion selective electrodes. Wu Guo-liang

/67/ has outlined methods of data treatment and diagramming, and discussed experimental techniques.

Ion selective electrodes are also used in automatic analysis /68/. The Kirin Institute of Applied Chemistry, Academia Sinica and Peking 5th Institute have attempted to apply electrodes to the control of production processes.

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PROGRESS OF ELECTROANALYTICAL CHEMISTRY IN THE PEOPLE'S REPUBLIC OF CHINA (1949 - 1979)

Part V

COULOMETRIC ANALYSIS

Coulometric analysis, especially coulometric titrations, have gained a new lease of life due to improvements in instrumentation in recent years. The main advantages of this method for analytical chemistry are connected with its unique ability to attain great precision and accuracy. This is because the ampere and the second, both of which are defined as basic SI units can be measured with a very high degree of precision. Whilst the Faraday constant, equal to 96487.2 A s g^{-1} $equiv^{-1}$ has an uncertainty of about 16 p.p.m., the current efficiency allows unequivocal interpretation of the process and the experimental performance of the method is sufficiently reliable for coulometric titrations to be claimed to give more precise results than any other procedure.

There were already many analysts engaged in research on coulometric analysis in the middle of the fifties in China /1/. But until 1963 their results /2/ were not described in formal domestic publications. During the past ten years or so much work has been done in this field by Chinese analysts. This is described briefly in the following paragraphs.

The study of new coulometric titrants

Zue Zong-Qi and Zhu pong-Ling /3/ studied the current efficiency for the electrogeneration of V(111) in a sodium acetate medium adjusted to pH=3 with hydrochloric acid at a mercury cathode. The experiments showed that the current efficiency for generating V(111) was 98.8% when a supporting electrolyte solution containing 0.2M vanadyl ion and a current density of 1.4 MA/cm^2 was used. Using a dead-stop end-point, they determined mg amounts of iron (111), vanadium (V), chromium (VI), and manganese (VII).

The above authors also studied the possibility of using electro-generated quinone /4/ and thallium (111) /5/ as coulometric titrants. The current efficiency for the generation of quinone from hydroquinone is close to 100% when a 0.25-5M H_2SO_4 solution containing 0.05M hydroquinone is used. With this titrant milligram amounts of titanium (111) and vanadium (11) can be titrated coulometrically with an average error about of 0.4%. Thallic ion electrogenerated from a solution containing a thallium salt in sulphuric acid at a platinum anode may also be used as a coulometric titrant. According to the current-voltage curve from the oxidation of thallous ion the optimum sulphuric acidity is 1M, where the current efficiency is close to 100%. Titanium(III) in the milligram range has been determined with an average error of 0.2%.

Yan Hui-Yu and Ren Hong-De /6/ generated pentavalent molybdenum as a coulometric titrant. The current efficiency for the electrogeneration of molybdenum (V) at a platinum cathode was found to be a function of the generating current density and the concentration of hexavalent molybdenum in various concentrations of sulphuric acid. With 4.5M sulphuric acid containing 0.1M ammonium molybdate the generation of molybdenum (V) is 100% efficient up to a current density of 1-10mA^{-2}cm. Milligram quantities of cerium (IV), chromium (VI) and vanadium(V) can be titrated coulometrically with an average error of about 0.2% or less. They found that copper (11) causes positive errors by catalysing the oxidation of molybdenum (V) by atmospheric oxygen and so purging with nitrogen was necessary. A potentiometric method was used for end-point detection.

Yan Hui-Yu and Xu Shao-Ling /7/ recommended tungsten(V) as a new coulometric titrant. The current efficiency for the electrogeneration of tungsten (V) has been evaluated as a function of generating current density and the concentration of hexavalent tungsten in various concentrations of sulphuric acid and phosphoric acid. The results obtained indicated that tungsten (V) was generated with 100% current efficiency by reduction of tungsten (VI) at a platinum cathode in a mixed solution of 1.5M sulphuric acid, 0.33M phosphoric acid and 0.4M sodium tungstate. A generating current density from 0.5 to 2.5 mAcm^{-2} can be used. A potentiometric method was used for end-point detection. Air must be removed by nitrogen from the test solution. This intermediate was used for the coulometric titration of manganese (VII), chromium (VI) and vanadium (V) from about 0.1 to 1.0 mg in a volume of 30ml. with an average error of 0.2%.

The study of analytical procedures.

Zue Zong-Qi *et al,* /8/ used the reaction of selenite and iodide to produce iodine followed by coulometric titration of the iodine with electrogenerated Sn(11). They determined the selenium in copper anodic mud with this method, and the results obtained are in agreement with that of gravimetric analysis.

Yan Hui-Yu *et al,* studied the coulometric titration of uranium /9,10/ and proposed a procedure to carry out the titration with electrogenerated manganese(111) and a ferric ion catalyst. It is convenient, rapid, and accurate. 1-5 mg of uranium may be titrated with an average error less than 0.2%. They also proposed a direct coulometric method at constant current for the determination of molybdenum(VI) with electrogenerated titanium(111). 0.1-5 mg of molybdenum can be determined with an average error about of 0.2% /11/.

Yan Hui-Yu and Zhu Xing-Yan /12/ ingeniously devised a procedure for the determination of tin by constant current coulometry. Tin(IV) is reduced by iron powder, and thus ferrous ion is produced in the cell. Tin(11) is titrated coulometrically with ferric ion which is produced at a platinum anode from ferrous ion. This process is convenient, economic on reagents, and increases the selectivity of the procedure for the determination of tin(11).

Chen Tong-Yue *et al,* /13/ studied the dual intermediates of coulometry using titanous ion as the reducing agent. Both current efficiency and titration efficiency of the titanous-bromine system are close to 100% in a solution containing 8M sulphuric acid, 0.1M sodium bromide and 0.6M titanium tetrachloride. The current efficiency for the generation of titanium(111) in a solution containing 0.2M citric acid, 0.1M ferric sulphate and 0.02M titanium tetrachloride may be close to 100% only after a pretitration is done because the background current of this system is high. Iron and O-nitrobenzoic acid have been determined in two systems separately and thorium determined indirectly by precipitation with o-nitrobenzoic cid.

Yan Hui-Yu *et al*, studied a method for the determination of chemical oxygen demand (COD) with dual intermediate coulometry. The oxidant Ce(IV) is generated in a saturated $Ce_2(SO_4)_3$ solution containing 1.2M HNO_3 and 1.5M H_2SO_4 to oxidize reducing substances in the water sample. The excess Ce(IV) is back titrated with electrogenerated Fe(11). The quantity of COD is calculated from a measurement of the electricity which is consumed by the water sample. The method can be used for the determination of COD in natural waters and waste water: The analytical results obtained may be compared with that of the permanganate method, but coulometry does not require a standard solution of $KMnO_4$, $H_2C_2O_4$ or Fe(11). It is a convenient, rapid and reproducible procedure, and suitable for automation. The coulometric titration of phenol /15/ and cyanide /16/ has also been investigated.

The application of coulometry in the monitoring of environmental pollution in China

According to the demand for environmental monitoring in China three kinds of analyzer have been manufactured by three units concerned under the leadership of the Beijing municipality.

Atmospheric nitrogen oxide analyzer /17/

This instrument uses galvanic coulometry. A flowing liquid cell was devised in which a platinum gauze was used as the cathode and the anode was made of active carbon. The electrolyte consisted of a 0.1M phosphate-buffered solution containing 0.3M Kl. While air is aspirate into the cell, the electrolyte is circulated continuously past the cathode. In the presence of nitrogen dioxide, iodine is liberated and then transported by the electrolyte to the cathode, where it is reduced. During the process, the electrolyte is regenerated, and a galvanic current flows. The current may be converted to the quantity of nitrogen dioxide according to Faraday's law if the efficiency of the galvanic cell is 100%. The following reactions are reported to occur in the cell.

$$2\ NO_2 + 2\ I^- \rightarrow 2\ NO_2^- + I_2$$

$$I_2 + 2\ e \rightarrow 2\ I^-$$

$$\cdots C + H_2O \rightarrow \cdots CO + 2H^+ + 2e$$

20ppb to 2ppm nitrogen dioxide can be determined automatically with this analyzer.

Sulphur dioxide and analyzer /18/

The detector is a coulometric cell with a platinum generating anode, a platinum gauze cathode, and an active carbon reference electrode. The cell is supplied by a constant current source and uses potassium iodide as the generating electrolyte, to generate iodine at the anode. The electrolyte is circulated continuously past the cathode,. The content of sulphur dioxide in the atmosphere can be determined directly from the current measurement of the reference electrode. The minimum detection limit is 0.05 mg/M^3, the precision is ca 5%, and the response time is about 5 minutes.

An automatic analyzer for determination of ozone and total oxidants in the atmosphere /19/

The principle of this analyzer involves the liberation of halogen by ozone or other oxidants from a phosphate-buffered solution of halides. The halogen congentration is determined galvano-coulometrically, i.e. by a differential measuring technique using a galvanic cell with two cathodes and a counter electrode. If ozone reacts with halides stoichiometrically and the resulting halogen is reduced at the cathode quantitatively the content of ozone would be proportional to the current of the galvanic cell, and may be calculated in accordance with Faraday's law. In order to determine ozone and total oxidants simultaneously, the air sample is divided into two equal streams before entering the measuring sections of the cell. The reducing agents are removed from both streams by chromium trioxide filters. A selective filter is used to remove ozone from one of the streams.

The analyzer can be used for the simultaneous determination of atmospheric ozone and total oxidants from 10ppb to 1ppm. with an average error about 5%. The response time is less than 5 min. and the background current is stable.

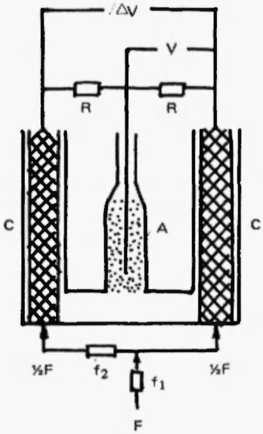

Fig. 1

Differential measurement of ozone and total oxidants. F,flow-rate of air sample; f, filter to remove reducing agent; f_2, filter to remove ozone selectively; C, cathode; A, anode.

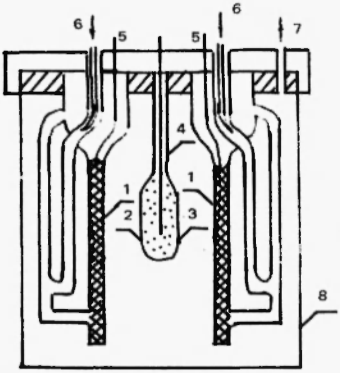

Fig. 2.

Details of construction of galvanic cell. 1.platinum gauze cathodes; 2.anode; 3.paste of activated carbon;4,5. platinum wire; 6.air inlet tube; 7.exhaust; 8.detector.

The three kinds of analyzer mentioned above have all been installed in the first batch of atmospheric pollution monitoring vans.

Applications of coulometric analysis in the petrochemical industry in China

With the development of the Chinese petrochemical industry, rapid, sensitive and accurate methods are required for the determination of many components in oil products.

Determination of sulphur

The petroleum institute of Fu-Shun /20/ devised a microcoulometer and determined sulphur in oil products by oxidimetry. The average error was about 5% for samples containing 0.2 to 10000ppm of sulphur. The Institute of Jing-men /21/ devised the model SKD-1 digital coulometric titrator. A quartz combustion tube in a controlled temperature heating oven was modified for suitable mineralisation of the organic sulphur. In this way they determined the total sulphur in crude oils, heavy petroleum distillation fractions and residues /22/. At present, this instrument has also been trial-produced in some other units in the PRC, such as Nan-Kau University, the Institute of Chemical Engineering of Shangsi, The Institute of Petrochemical Engineering Science and the Second Factory of Analytical Instruments of Shanghai, etc. The microcoulometric determination of sulphur has gradually been perfected with respect to methodology and instrumentation.

Determination of nitrogen

Since Martin /23/ applied microcoulometry to the determination of total nitrogen in oil in 1966, many analysts in factories and laboratories have successively accepted this method. In recent years, a large number of studies have been carried out on catalysts, absorption of acidic gases and the processes of electrode reactions, etc. Some work has also been done in the fields mentioned above by some units of the petrochemical departments /24,25/ in China. The Institute of Jing-men determined the total nitrogen in oil products microcoulometrically by using a Ni-MgO hydrogenation catalyst /26/. They determined 0.5 to 1000ppm of nitrogen in the oil fraction below 350°C. The determination error was less than 5% for samples containing more than 10ppm of nitrogen.

Coulometric determination of bromine value

The contents of olefines in oil products have become an important index for the quality of oil products and process control in production. The unsaturated fraction of oil products is usually characterised by the bromine value. In recent years, the bromine value has been determined coulometrically and some of these methods have now been accepted as standard ones. A lot of work in this field has been done in several units /27-30/ in China. According to experimental results, this method can be applied to the determination of bromine index and bromine value within the range of 0 to 1000 and 0 to 100, respectively, in fractions of gasoline, kerosene, and diesel oil. The precision of these methods meets the Standard Sy 2123-77. It takes only 3-5 minutes for each process and requires only a 10 litre sample solution when the bromine value is about 1. Therefore, 60ml electrolyte can be utilized several hundred times, and it also avoids the use of mercuric chloride and methyl alcohol, etc. Compared with ordinary titrimetry this method has the advantages of simplicity, rapidity and high accuracy. As a result, it can be regarded as a reliable analytical method for the identification of petroleum products and control analysis in engineering processes.

Determination of water in petroleum products

Coulometric titration has been widely employed in the determination of water in petroleum products. This method was first suggested /31/ and improved later /32/ by Meyer. Since coulometric titration is carried out by electrogeneration of iodine in organic solutions containing iodide, pyridine and sulphur dioxide, as long as the current efficiency for electrogeneration of iodine is 100%, the content of water in the sample can be calculated directly by Faraday's law, without frequent standardization of reagents. At present, this method has found wide applications /33-36/ in China. For example, micro-quantities of water in crude oil /33/ may be determined by a coulometric titration, in which the average error is less than 5% for samples containing more than 10ppm of water and it requires only 3-5 minutes to perform several analytical measurements. Another satisfactory example, is the coulometric titration of water in light oils, lubricants and oil additives.

Applications of coulometric titration in the identification of purity of reagents

In order to evaluate primary standards for titrimetric analysis to meet the needs of scientific research and production, the National Institute of Metrology of China has applied precision coulometry to establish the purity of potassium acid phthalate, sodium carbonate, potassium dichromate, arsenic trioxide and sodium chloride. The results obtained are compared with the related data abroad and are listed in Table 1.

Table 1 - Results of identification of purity of some reagents

Reagents	Standard deviation %		
	America	Japan	China
potassium acid pthlate	0.003/37/	0.036/38/	0.007/44/
sodium carbonate	0.007/37/	0.044/38/	0.004/44/
potassium dichromate	0.003/39, 40/	0.014/38/	0.002/45/
arsenic trioxide	0.0032/41/	0.021/38/	0.003/44/
sodium chloride	0.0037/42/	0.037/43/	0.005/44/

There are many other examples of the application of coulometric titration that might be mentioned, e.g. coulometric titration of the element of Kuduz vine roots, /46/ determination of small amounts of carbon in niobium and tantalum by coulometry /41/, determination of iron in aluminium /48/, determination of oxygen in rare metals and alloys by coulometry /49/, determination of trace amounts of sulphur in silicon and silicon dioxide /50/, etc. Because work on coulometric analysis was developed later in China than elsewhere, its application has not yet become widespread. With further development of scientific research and production in China, it is expected that coulometry will find much wider applications because of its accuracy, sensitivity, simplicity and rapidity and because it is easily automated.

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