

2. The $\dot{\text{N}}\text{H}_2$ and $\dot{\text{N}}_2\text{H}_3$ radicals have been found to undergo recombination in solid ammonia and hydrazine under the action of ultraviolet light. The $\dot{\text{O}}\text{H}$ radicals react with NH_3 molecules at the temperature of liquid nitrogen under the action of ultraviolet light, with the formation of $\dot{\text{N}}\text{H}_2$ and $\text{H}\dot{\text{O}}_2$ radicals.

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APPARATUS FOR MEASURING THE EXCHANGE CURRENT AND THE TRUE RATE OF THE ANODIC PROCESS ON AMALGAM ELECTRODES WITH THE AID OF RADIOACTIVE ISOTOPES

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In recent years radioactive isotopes have been widely used for investigating the kinetics and mechanism of electrode processes, especially the ionisation of metals and the discharge of metallic ions. The radiochemical technique enables the rate of a given electrode process at equilibrium (exchange current) to be measured even when the corresponding reverse process predominates. A method has been developed to do this with amalgam electrodes, based on a combination of electrochemical and radiochemical measurements, which are made by periodic monitoring of the radioactivity of a solution in contact with a labelled amalgam, under conditions such that the transfer of radioactivity from the solution back to the amalgam may be neglected¹. This method allows systems with relatively low exchange currents to be investigated, since a certain time is taken up in withdrawing, measuring, and returning the samples, and not less than 4 or 5 samples have to be taken to plot a reliable curve of the rise of radioactivity with

time. What is more, with rapid electrode processes there is an inevitable increase in the errors due to insufficiently accurate determination of the instant of taking the sample and of the duration of the radioactivity count, to the impossibility of carefully cleansing the counting chamber from the remnants of the past sample, etc.

In order to eliminate these shortcomings, and also to achieve automatic recording of a rapid rise in the radioactivity of the solution with time, we have developed a new design of measuring cell with circulation of the solution through a side-tube†; for the continuous recording of the radioactivity of the solution in this tube and the automatic tracing of its variation with time, we have built a special counter apparatus based on commercial electronic instruments, consisting of a combination of a scintillation counter with an integrating device and an electronic pen-recording potentiometer.

Fig. 1 shows the layout of the cell. In the upper part of the cell 1 the tracer-containing amalgam was prepared by electrolysis. The amalgam was allowed to flow into the central cell 2, in which the experiment was conducted. The cell was provided with double walls, between which was circulated water from a thermostat. The side cell 3 contained a platinum auxiliary electrode 4. The end of the tube connecting 2 and 3 was brought out to the centre of the cell; together with the formation of a funnel-shaped depression in the surface of the amalgam on stirring, this ensured even distribution of the lines of force when the amalgam was polarised. The burette 8 served for introducing various additional substances into the central cell. The electrolyte bridge 7, with a porous glass membrane sealed into its tip, led down to the surface of the stirred amalgam.

The glass stirrer 5 was accurately centred; the bottom end of its axis was supported in a depression in the base of the cell, while its top end rested in a special cap fused to the tube for transfer of amalgam from the upper cell. In the lower part of the stirrer an iron rod was sealed into the glass tube. A horseshoe magnet under the cell was used to rotate the stirrer, the speed of rotation being monitored by means of a stroboscopic disc fixed to the magnet.

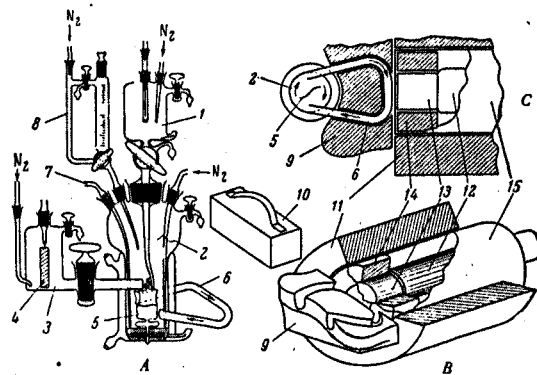


Fig. 1. Layout of apparatus: A) glass cell; B) protective chamber with scintillation counter; C) plan of lower part of cell 2 and protective chamber.

† Our thanks are due to V. S. Zimin for his help in the design and manufacture of the cell.

The stirrer performed several functions. Its lower part carried two pairs of propeller-type blades designed to agitate the amalgam and the solution. The broad upper blade of the stirrer, whose top part was S-shaped in plan, forced the solution in the direction shown by the arrow (Fig.1), and ensured a continuous circulation of the solution through the side-tube 6, which served to remove continuously part of the solution from the central cell so that its radioactivity could be measured. In order to assess the rate of circulation of solution through tube 6, measurements were made of the time for the front of a coloured liquid to pass through the whole tube; this time was 3 sec for a tube 11 cm long and 0.3 cm in cross-section. For assembly the cell was mounted in such a way that the circulation tube fitted into a corresponding groove cut in the lead protective screen 9, so as to match up the linear section of the tube with the window in the body of the sensor 15 containing the scintillator 13.

A scintillation apparatus was used for continuous recording of the γ -radiation, based on a Tyul'pan intensimeter, a Tiss radiometer, and a modified TI sensor containing a crystal of NaI(Tl) (40 mm in diameter and 40 mm long) (Fig.2). The sensitivity of the apparatus was $3.6 \text{ count} \times \text{min}^{-1}$ at $10^{-11} \text{ c ml}^{-1}$ (for $E_\gamma = 1.1 \text{ MeV}$). The count rate (less the background) was $25000 \text{ pulses min}^{-1}$ when a solution of specific activity $7 \times 10^{-8} \text{ c ml}^{-1}$ was circulated through the tube. The background γ -radiation of the apparatus was $250\text{--}500 \text{ pulses min}^{-1}$. The lead bushings 9 and 10, housing 11, and screen 14 (Fig.1) of effective thickness 50 mm ensured the necessary reduction in the background due to cosmic radiation and the radioactivity of the amalgam. The pulses from the TI sensor were fed to the input of the "Tyul'pan" after passing through a 1.1 Mohm resistor, which reduced their amplitude as necessary†, and a discriminator (a DGTs-7 germanium diode). The Tiss radiometer was used to supply the probe unit of the "TI". An EPP-09 pen-recorder connected directly to the "Tyul'pan" was used for recording the activity. The voltage at the EPP-09 input was supplied from an R-14 resistance box. Another R-14 resistance box connected in series with the input of the EPP-09 provided a loading of 820 ohm for the "Tyul'pan" microammeter circuit. The non-linearity of

the "Tyul'pan" scale for uniformly incident pulses is not greater than 3%. The reading error due to dead time in the "Tyul'pan" is 0.8% for the $15000 \text{ pulses sec}^{-1}$ scale, and not more than 2.5% for the $50000 \text{ pulses sec}^{-1}$ scale.

In order to simplify the design of the apparatus and extend its limits of measurement towards higher count rates, the following improvement has recently been made. The Tyul'pan instrument has been converted by a simple modification into a scintillation radiometer. For this purpose it has been fitted with a high-voltage rectifier whose output is controllable from 0 to 2000 V. The rectifier is assembled as a voltage-quadrupling circuit. The rectifier high-voltage winding is wound on the former of the "Tyul'pan" power transformer. In order to monitor the high-voltage setting, the microammeter can be switched by means of a changeover switch from measuring the count rate to measuring the high voltage. The connector designed for use with the cathode-follower probe is used with slight modification to connect in the scintillation sensor: the high voltage is brought out to it, and the supply leads are reterminated according to the pin-numbering of the sensor plug. The γ -sensor may use an FEU-24, FEU-19M, or FEU-29 photomultiplier. In the first case single crystals of NaI(Tl) 70 mm in diameter and 40 mm long can be employed. To prevent pulse superimposition at count rates up to $5 \times 10^4 \text{ pulses sec}^{-1}$, the photomultiplier load is reduced to 10 kohm.

The above apparatus allows variations in γ -radiation intensity to be recorded during rapid processes occurring in very short time intervals ($\sim 0.1 \text{ sec}$). By setting up a relatively high specific activity in the amalgam, we can determine the rate of isotopic exchange during the initial period, when the reverse process of transfer of activity from solution to amalgam can be neglected, and the radioactivity of the solution increases linearly with time.

The technique described above has been used for studying the electrode processes on amalgams of indium and zinc². For an experiment a radioactive amalgam of the metal in question was prepared by electrolysis in the cell 1 (Fig.1). The completeness of deposition was verified by measuring the residual radioactivity of the solution. At the same time a known volume of acidified sodium perchlorate solution, which was used as an indifferent electrolyte, was saturated with nitrogen in the cell 3 and freed from surface-active impurities on the activated platinised platinum electrode 4. The amalgam was run under pressure into the cell 2, which was filled with nitrogen§, and then the solution from 3 was admitted (at the instant when the solution touched the amalgam a slight cathodic polarisation was applied), and the electrolyte bridge 7 was inserted. After this the stirrer was started and the background recorded. Then the cathodic polarisation was switched off, and a known volume of a solution of a non-radioactive salt of the metal was added from the burette 8; the curve of rise in radioactivity I against time t was recorded at the equilibrium potential (exchange current) and one or more such curves were taken at various anodic polarisations (anodic points).

Fig.3 shows the recording from one of these experiments with an indium amalgam (total activity 0.1 mc) and $\text{In}(\text{ClO}_4)_3$ solution. The horizontal line shows the background level

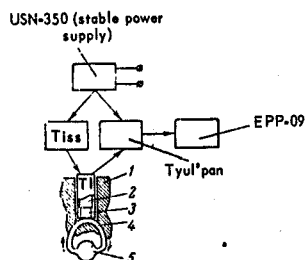


Fig. 2. Block diagram of apparatus: 1) lead screening; 2) FEU-19 photomultiplier; 3) NaI(Tl) scintillator; 4) glass circulation tube; 5) cell.

† The sensor probe was disconnected, and the input of the Tyul'pan instrument was shunted by an equivalent resistance of 4.3 k Ω .

§ The tap connecting 1 and 2 was provided with a special draw-off tube, which made it possible to blow nitrogen through the internal part of the tap to expel the amalgam.

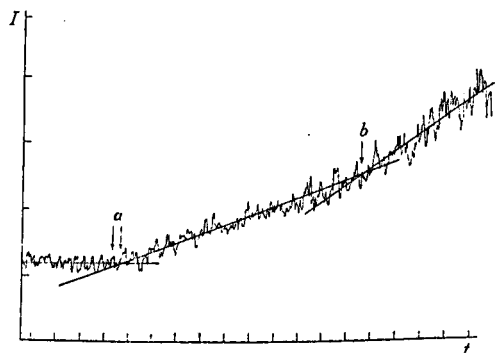


Fig. 3. Curves of rise of radioactivity with time for indium amalgam.

before the start of the exchange, while the arrows at point *a* correspond to the beginning and end of the inflow of solution from the burette. Point *a* corresponds to the start of the exchange between solution and amalgam at the equilibrium potential, and point *b* to the instant of applying anodic polarisation. The exchange current and the true rate of the anodic process were calculated by the procedure described previously¹. The maximum error in determining the slope of the *I*-*t* curve did not exceed 3%. The recording of an anodic radiochemical point far from the equilibrium potential makes it possible to determine the exchange current also directly from a comparison of the slopes of the *I*-*t* curves for the anodic point and for the exchange current, and also to find the current efficiency of the anodic dissolution of indium. The presence of the burette allows the same experiment to be used for measuring the exchange current with variation of the metal ion concentration in the solution, and also for studying the effects of various additions, e.g. surface-active agents, halide ions, etc.

As well as the measurement of exchange currents and true rates of electrode processes, the technique described above permits a very highly sensitive study to be made of the formation and dissolution of amalgams and their dependence on various factors (potential, current, composition of solution, temperature); it may also be used for measuring rates of electrode processes, and under certain conditions exchange currents at solid electrodes². In particular, because of its very high sensitivity this technique may be used also for studying the corrosion and anodic dissolution of passive metals and alloys (which proceed at very low rates), provided that the products of corrosion are soluble.

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A CHROMATOGRAPHIC COLLECTOR WITH CAPACITANCE PICK-UP

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In our previous work¹ we have described collectors with photoelectric dosimeters. On further investigation an instrument with a capacitance dosimeter has proved to be of interest and also economical in its electricity consumption, since it contains no light source. Receiver transport is achieved in the same way as in the vertical sampling device. In this model the opening and closing of the dosimeter valve is brought about not by an electromagnetic device but by a mechanical drive from the motor that replaces the receivers. The electrical circuit and the kinematic layout are shown in the Figure.

The radiofrequency oscillator is designed as a Hartley circuit using the transistor VT1. The inductor *L* and the capacitor *C* form the tuned circuit of the oscillator. The resistor *R* is connected to the circuit LC through capacitor *C*₄. When the capacitance *C*_x is a minimum (liquid level not reaching the capacitance sensor), the amplitude of oscillation in circuit LC is a maximum, as is also the current through VT1. This current, after amplification by a second transistor VT2, operates the relay RL, which has contacts 1 open and 2 closed. As the capacitance *C*_x increases, so does the shunting effect of *R*. This leads to a fall in the current through VT1 and hence in the current through relay RL.

