Possibility of utilizing electrochemical techniques for the evaluation of the content of organic impurities in water*

A. DE BATTISTI,

Chemical Institute, Instrumental Chemical Analysis, the University, Ferrara, Italy

L. FORMARO and S. TRASATTI

Laboratory of Electrochemistry, the University, Via Venezian 21, 20133 Milan 5, Italy

---

The use of some special electrochemical techniques, such as the measurement of the double layer capacitance and the determination by fast charging curves of the fraction of electrode surface covered with adsorbate, is proposed as a powerful tool for the evaluation of water quality with respect to organic pollution. Principles of the method are described in detail and practical possibilities are exemplified which make use of simple organic substances. The sensitivity of the method in relation to the nature of the electrode used, as well as of the kind of impurities in solution, is discussed. As a practical application, the method is used for the evaluation of the quality of industrial waters coming from demineralization beds and boilers as well as of laboratory waters prepared with different chemical and electrochemical treatments. This method enables impurity contents as low as 0·01 p.p.m. to be detected. However, if the reference purity could be that of water treated with active charcoal, then the sensitivity of the method could be greatly increased and the lower limit would become ideally pure water.

---

1. Introduction

The problem of the control of the purity of water is especially relevant to the laboratory research where it is necessary to work with such pure base solutions as not to affect experimental measurements [1]. However, this problem may also be faced in the industrial field where the water quality required may, in comparison, appear not very high, but where it must be kept below rather sharp upper limits above which the lifetimes of the plants can be compromised. This is particularly true in the case of the steam system of an industrial plant including, besides the boiler which is the vital organ, stills, heaters, regenerators, in short all parts where heat exchange may occur.

Impurities in water can consist of both organic and inorganic materials. Inorganic impurities will not be dealt with in this paper, for several sensitive, precise methods are available for their detection [2]. Attention will be focused here on the organic pollution which very often is, or must be kept, at a level below the sensitivity of current analytical methods. In fact, if in the boiler the organic impurity level must be below 10 to 20 p.p.m., the impurity content in feed water for re-cycling must necessarily be kept fifty to a hundredfold lower. Now, titration with permanganate allows evaluations down to 10 ± 2 p.p.m.†, while the use of an infrared analyser of

* Paper presented at the National Congress of Analytical Chemistry, October 16–18 1973, Ferrara (Italy).

† The impurity concentration is throughout expressed as carbon content.

the CO_2 formed in the oxidation with O_2 of the carbonaceous material present in water allows a sensitivity of 1–2 p.p.m. with an accuracy of 20% at these pollution levels [3]. The latter methods present some inconvenience as regards the possible distinction between organic and inorganic carbonaceous materials. In some rare cases where no volatile organic materials are present, sample concentration may allow the practical sensitivity to go down to about 0·1 p.p.m. [4].

The above methods, while possibly useful in some cases of industrial water, never ensure the sensitivity required to evidence the pollution of laboratory water. They are often unsuitable also for industrial water, for instance in the case of water for re-cycling coming from demineralization beds.

In this paper the possibility of exploiting electrochemical techniques for the evaluation of pollution levels in water is discussed. As will be shown, the proposed method is capable of providing evidence of organic contents as low as 0·1 p.p.m. The most interesting feature is that the sensitivity is at a maximum in the range 0·01 to 10 p.p.m., precisely where the other available analytical methods appear to fail.

2. Principles of the method

The method relies on the adsorption equilibrium at the solid/liquid interface. Consider an aqueous solution containing an organic impurity. If a solid/liquid interface is created by immersing a solid body, the organic substance will adsorb at the phase boundary following a sort of partition law [5]. The phenomenon is particularly marked in the case of metallic surfaces and it can also be governed by polarizing the metal [6]. The adsorption equilibrium established at the metal/liquid interface is expressed by *adsorption isotherms* which are relationships between Γ, the concentration of the organic substance at the interface (mol cm^{-2}) and c, the concentration in the solution bulk. In a quite general way, the adsorption isotherm may be written in the form [7, 8]:

$$F(\Gamma) = \beta c \qquad (1)$$

where β is a constant at constant electrical state of the interface. β is termed the *adsorption*

coefficient and to a first approximation may be identified with the equilibrium constant of the adsorption process. β is therefore directly related to the free energy of the reaction. For our purposes Equation 1 may be reduced to:

$$\Gamma \propto c \qquad (2)$$

which strikingly evidences the possibility of exploiting adsorption isotherms for analytical purposes. To a first approximation, the determination of Γ is sufficient to derive c.

In practice, the procedure cannot be so straightforward. In fact, apart from in a few cases*, a direct experimental determination of Γ cannot be accomplished. However, it is possible to determine, either directly or indirectly $\Gamma/\Gamma_s = \vartheta$, i.e. the degree of coverage of the metal surface with adsorbed organic substance, Γ_s being the saturation surface concentration. Equation 2 can thus be rewritten in the form:

$$\vartheta \propto c \qquad (3)$$

A further point to consider is the necessity of a calibration curve, because the proportionality constant in Equation 3 is unknown. This means that this is in practice a relative and not an absolute method. However, this does not reduce its usefulness. In fact, if the substance to be analysed is known, the establishment of the calibration curve is straightforward, whereas if just the general organic content is to be evaluated, then the pollution level can be deduced from a comparison with a *blank* made up with ultra-pure water prepared in the laboratory. However, it must be noted that comparison between two water samples containing the same kind of impurity is rigorously quantitative, whereas any comparison between water samples differently polluted can only be qualitative. This results from the fact that, in general, different β values pertain to different substances, so that the same value of c need not correspond to the same value of θ.

Lastly, as the method is electrochemical in nature, it is necessary to make the water electri-

---

* For example, Γ can be easily obtained from interfacial tension and capacity measurements for liquid metals (Hg) [9]. Radiotracer techniques enable such measurements to be extended to solid metals in some cases [10].

cally conducting in order to carry out the analysis Generally, water samples are made 0·1 to 1 M in $HClO_4$. ClO_4^- ions are known to be weakly adsorbed on electrodes [11] and this keeps any interference with the surface phenomenon due to organic impurities at a minimum.

From Equation 3, the present method is seen to be experimentally based on the determination of ϑ. This can be accomplished in two ways, one indirect and the other direct. Correspondingly, two electrochemical techniques can be used.

2.1. Indirect route. Measurement of the double layer capacity.

The interface between an electrode and an electrolytic solution behaves as an electric condenser [9, 12]. The capacitance of this condenser can be measured experimentally with a bridge [13–15] or with the single galvanostatic pulse method [16, 17]. Let C_0 be the capacity at a given electrode potential in the absence of pollution. After adding an organic substance to the solution, its adsorption will occur by the replacement of the solvent molecules orginally present at the interface. This is formally equivalent to the substitution of the dielectric in a condenser [12]. A decrease in C_0 will occur on account of the generally larger size and lower dielectric constant of organic substances with respect to water. The lower value, C_1, will correspond to the saturation of the electrode surface with adsorbate.

At constant potential and in the potential range where adsorption is most pronounced, the following equation holds to a satisfactory approximation [12]:

$$\frac{C_0 - C_\vartheta}{C_0 - C_1} = \vartheta \qquad (4)$$

where $C\vartheta$ is the capacity at the coverage ϑ. Since C_1 is not always measurable in an unequivocal way, but is, however, a constant for a given substance (or for a given kind of pollution), from Equation 3 and 4 we may write:

$$(C_0 - C_\vartheta) \propto c \qquad (5)$$

It results from Equation 5 that it is in principle possible to build up calibration curves or evaluate organic pollution simply from the extent of the decrease in the capacitance of the electrode/solution interface.

2.2. Direct route. Fast galvanostatic pulses

This technique can be applied only to metals of the Pt group. If a cathodic galvanostatic pulse is applied to a Pt electrode after a suitable potential sequence to condition its surface (see later), the electrode potential changes in a characteristic way with time before attaining the value corresponding to the hydrogen evolution reaction (Fig. 1a). This portion of the charging curve refers to the formation of a monolayer of atomic hydrogen on the surface [18, 19]. From the value of the applied current density and the value of the transition time, τ (Fig. 1), the quantity q_H^s is derived, namely the charge needed to saturate the surface with hydrogen.

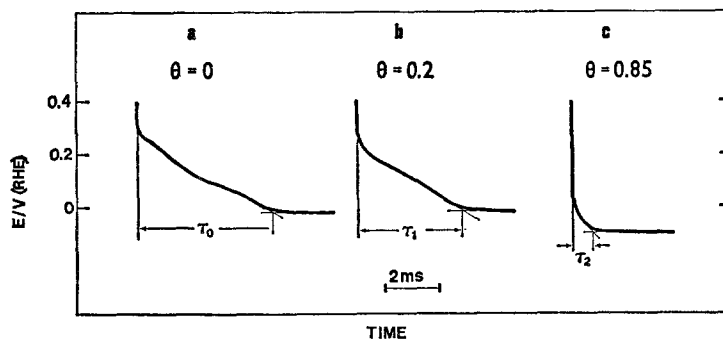When the surface is partly covered with or-

Fig. 1. Decrease in the hydrogen adsorption region of cathodic charging curves for Pt in 1M $HClO_4$ solutions duet to parallel increase in the fraction of surface (θ) covered with adsorbed organic impurities.

ganic substance, some sites cannot be used for the deposition of hydrogen and τ will decrease (Fig. 1b, c). From the relation:

$$\frac{q_H^s - q_H}{q_H^s} = \vartheta \qquad (6)$$

the fraction of surface occupied by organic molecules can be obtained.

It is of interest to note that this technique and the determination of capacitance by the single galvanostatic pulse method require precisely the same equipment. The difference between the latter technique and the bridge method is that it is impossible to follow the decrease in C with time (if necessary) when a hand-balanced bridge is used. However, the bridge ensures much higher accuracy.

3. Kinds of electrodes

The choice of metal to use as the indicator electrode depends on several factors, such as the possibility and reproducibility of measurements of C and q_H. The capacitance of the double layer at the metal/solution interface can be measured easily on Hg but, among solid metals, it can be measured with sufficient accuracy and reliability only on metals of the Pt group [20]. In contrast, q_H measurements are performable only on Pt metals [21, 22]. The choice is ultimately restricted to Pt and Hg inasmuch as the other metals of the Pt group show some overlapping between the range of potential where oxygen and hydrogen are adsorbed [21, 23], which complicates somewhat the interpretation of experimental data.

An important experimental point is the need for a renewable electrode surface. This is a further factor which restricts the possible choice to Pt and Hg. In fact, Hg surfaces are known to be easily restored by dropping, while an electrochemical pre-treatment, such as that shown in Fig. 2, can be used for Pt [13, 22]. In this case, organic substances possibly pre-adsorbed on Pt surfaces can be removed by bringing the electrode potential to values around 1·5 V (RHE), where the adsorbate is oxidized as the surface becomes covered with a monolayer of adsorbed oxygen. If the potential is then brought to a value close to the hydrogen evolution, the oxide layer is
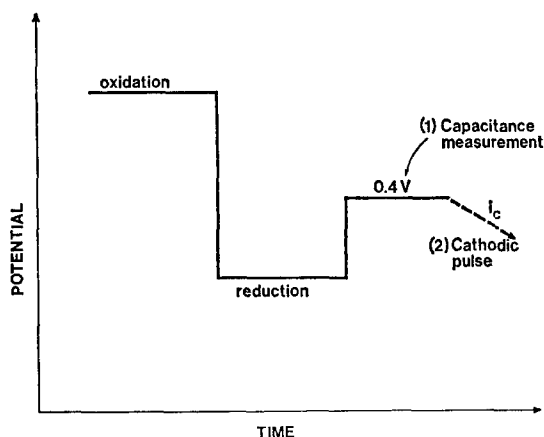

Fig. 2. Sketch of the potential/time sequence used to pre-treat the Pt electrode surface before adsorption measurements.

rapidly reduced within a few milliseconds and substituted by a monolayer of atomic hydrogen. Finally, bringing the potential to 0·4 V where atomic hydrogen is quickly ionized, leaves a perfectly clean surface in a reproducible controlled state. Neither hydrogen nor oxygen is adsorbed on Pt at 0·4 V [22, 24]. Thus, after each adsorption measurement, it is sufficient to apply to the metal the potential/time sequence of Fig. 2 to restore the surface and to make the electrode ready for a new measurement.

A further important point is that the presence of oxygen dissolved in solution does not affect this type of measurement, so that degassing is not needed and any risk of removing volatile impurities in this way, is avoided. Moreover, effects due to inorganic carbonaceous materials are negligible. Therefore this method is highly selective with respect to organic carbon.

Further experimental details can be found in previous publications [13, 18, 24, 25].

4. A practical example

The adsorption of glycol aldehyde, which interacts very strongly with the surfaces of Pt electrodes, is used by way of a practical illustration. Fig. 3 shows capacity/potential curves for a platinum electrode in solutions containing various amounts of glycol aldehyde. The capacity of the double layer, C, can be seen to decrease with increasing concentration of the organic substance, particularly around 0·4 V,
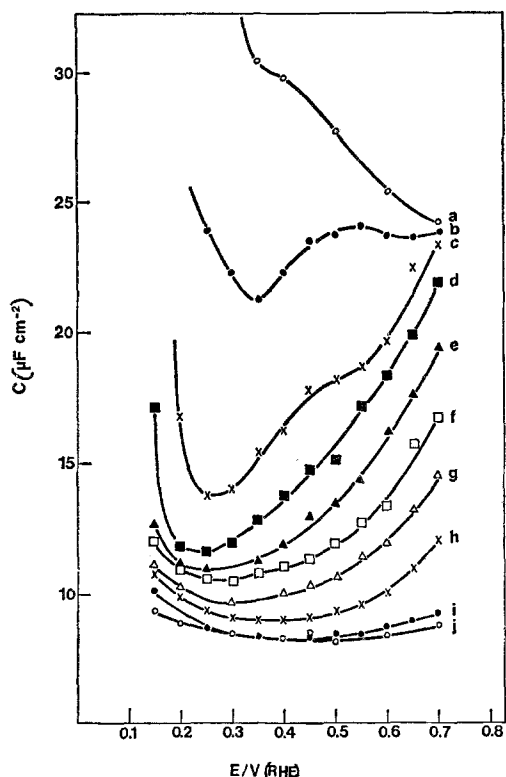
Fig. 3. Capacity/potential curves at 25°C for Pt in 1 M HClO$_4$ solutions containing increasing amounts of glycol aldehyde. Adsorption time, 3 min. (a) 0; (b) 10^{-5}; (c) 3·3 × 10^{-5}; (d) 10^{-4}; (e) 3·3 × 10^{-4}; (f) 10^{-3}; (g) 3·3 × 10^{-3}; (h) 10^{-2}; (j) 10^{-1} M.

the starting value in the absence of any organic addition is indicated by C_0.

The coverage of the surface with adsorbed glycol aldehyde at 0·4 V has been derived from Fig. 3 with the aid of Equation 4 and has also been measured directly by cathodic pulses making use of Equation 6. Fig. 4 compares the two sets of ϑ values as a function of the concentration of glycol aldehyde expressed as mol l^{-1} as well as carbon content. The two experimental techniques give exactly the same adsorption isotherm. There exists clearly a linear relationship between θ and log c (Temkin isotherm [26]) which can be employed as a calibration curve. We see that the range of applicability of this method for this substance extends from 0·01 to about 100 p.p.m. Beyond the latter value the electrode surface becomes saturated and the capacity of the double layer does not vary with concentration.

5. Sensitivity of the method

The sensitivity of this method depends on a number of factors which, though interrelated, will be discussed separately for the sake of clarity.

5.1. Nature of the electrode

This governs the value of β (in Equation 1) to which sensitivity is directly proportional. From this point of view, Pt turns out to be

down to a lower value which remains constant even if the concentration is further increased. This is the value indicated above by C_1, while
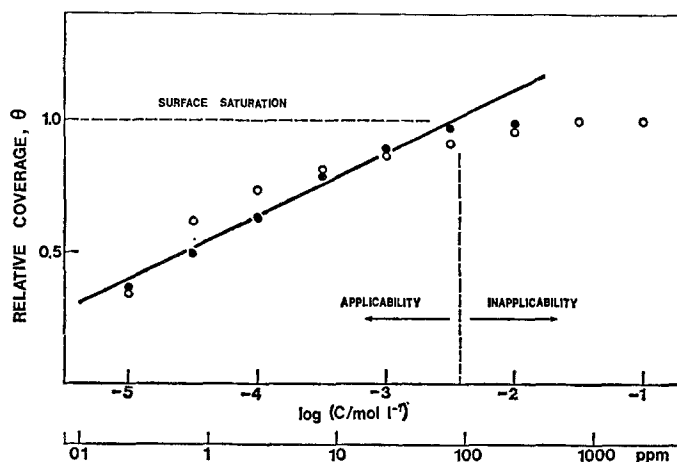

Fig. 4. Isotherm (calibration curve) at 25°C for glycol aldehyde adsorption on Pt from 1 M HClO$_4$ solutions. (○) Capacity data; (●) Charging curves data.
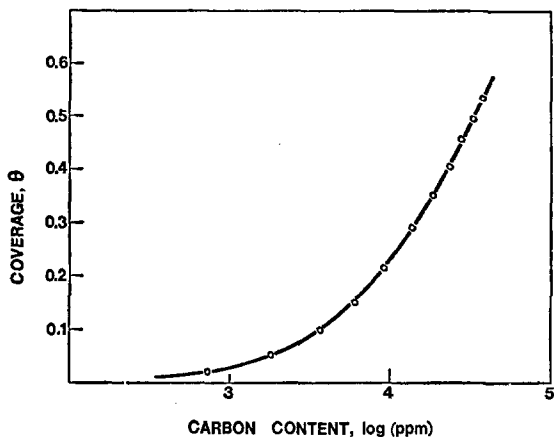
Fig. 5. Isotherm (calibration curve) at 25°C for acetonitrile adsorption on a dropping Hg electrode from 0·25 M NaF solutions.

strongly favoured with respect to Hg. In fact, except for a few cases of chemisorption [8, 27], adsorption of organic substances on Hg is physical in nature [12, 28, 29] with ΔG_{ads} only amounting to a few kcal mol^{-1}. Fig. 5 shows an isotherm at about $-0·4$ V (versus SCE) for the adsorption of acetonitrile on Hg. Ethylene glycol gives almost identical results [30]. It can be seen that the sensitivity with Hg is much lower than that with Pt. In fact, it is impossible to detect with Hg amounts below 1000 p.p.m., whereas ethylene glycol adsorbs on Pt with an isotherm [31] identical to that for glycol aldehyde. The times necessary to attain adsorption equilibrium can also lead to problems in the

case of dropping mercury electrodes. Hanging Hg drop electrodes could be used in these cases [32], but from all points of view Pt electrodes are more satisfactory.

5.2. The value of β

The value of β is exponentially related to the free energy of adsorption.

Large differences in β can sometimes be observed for various substances adsorbing on Pt electrodes. This is certainly the case for some substances containing the carboxyl group (oxalic acid, glycolic acid etc.). While most of the organic substances undergo dehydrogenation and chemisorption on Pt electrodes [33], the above acids do not lose hydrogen on adsorption [34, 35]. This gives rise to a lower value of β and thus a lower sensitivity (see case of oxalic acid in Fig. 6).

5.3. The role of the 'blank'

The purity of the reference water ('blank') directly affects the sensitivity. In the case of the adsorption of glycol aldehyde illustrated above, solutions were made up with triple-distilled water. The value of the capacity for Pt immediately after the surface pre-treatment [24] is about 34 μF cm^{-2}. However, this cannot be taken as the reference value C_0, because, owing to the slowness of the organic material adsorption
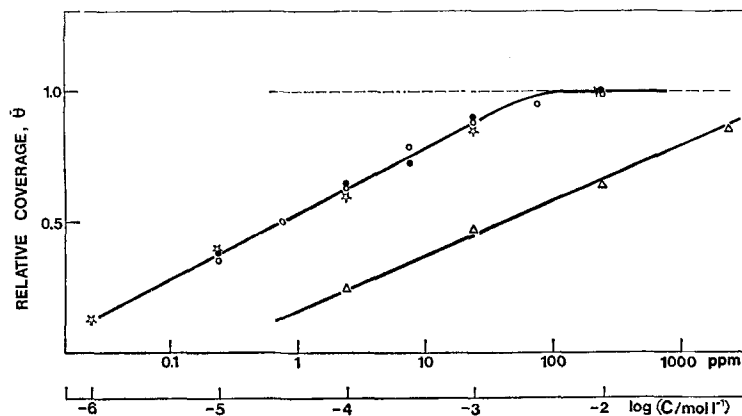

Fig. 6. Isotherms (calibration curves) at 35°C for the adsorption of various organic substances on Pt from aqueous solutions of surface inactive electrolytes. (●) Glyoxal; (○) glycol aldehyde; (★) ethylene glycol [31] (△) oxalic acid

process, it takes some time to attain equilibrium. For this reason, capacity readings were taken 3 min after the application of the potential/time sequence for cleaning the surface. During this time, co-adsorption, though limited, of glycol aldehyde and impurities originally present in the 'blank' will take place. Thus the value of C_0 to be used in Equation 4 should be that measured with the 'blank' under the same experimental conditions as those used for the subsequent measurements. In the particular case of Fig. 3 we see that the value of C_0 (i.e. the value of C measured 3 min after the application of the pre-treatment sequence) for the given 'blank' is about 29 μF cm^{-2}.

The maximum sensitivity would be obviously obtained in ultra-pure water for which C_0 should change with time. Although this may be practically realizable [36] (filtration through active charcoal) no convenience would result therefrom in practical cases where the ultra-pure water would unavoidably come into contact with the atmosphere. For this method, it is therefore sufficient to use double-distilled water which should be stored under nitrogen. This very simple arrangement has been found to give water with impurity contents within rather narrow limits.

The relative impurity levels of 'blanks' can be assessed from q_H values and their dependence on time. As an example, Table 1 shows the fraction of electrode surface covered with impurities at the given times after activation for a 1M HClO$_4$ solution and two 1M H$_3$PO$_4$ solutions, respectively. The two H$_3$PO$_4$ solutions

differ in that the former was made up with concentrated H$_3$PO$_4$ taken as such from the bottle, whereas the latter was prepared from concentrated H$_3$PO$_4$ refluxed overnight with H$_2$O$_2$. Table 1 clearly shows that the measure of q_H is a powerful tool to evidence the degree of purity of a solution.

A linear relationship between q_H and $t^{1/2}$ shows that impurity adsorption is diffusion-controlled. From the well-known equation:

$$i_{diff} = FDc/\delta \qquad (7)$$

where $i_{diff} \cdot t = \Delta q_H$, F is the Faraday constant, and assuming for D a reasonable average value of 10^{-5} cm^2 s^{-1} and for δ, the diffusion-layer thickness, a value of 0·01 cm in quiescent solution, the impurity concentration can be estimated to be of the order of 10^{-7}–10^{-6} equiv. l^{-1}. This can be regarded as the level of impurities of a water in equilibrium with a 'normal' laboratory atmosphere in agreement with other authors [37–39].

It is advisable not to try to measure experimentally ϑ values lower than 0·2–0·3 inasmuch as the influence of the 'blank' at these levels is not negligible. It is best in these circumstances to extrapolate the calibration curve itself to the lower concentrations (the ϑ versus log c relationship is usually linear [33] down to about $\vartheta = 0·1$).

6. Selectivity

It is clear that this method is not selective as regards different organic substances, which is also true of other analytical methods which are

Table 1. Fraction % of electrode surface covered with impurities after the given time t at 0·4 V (RHE).

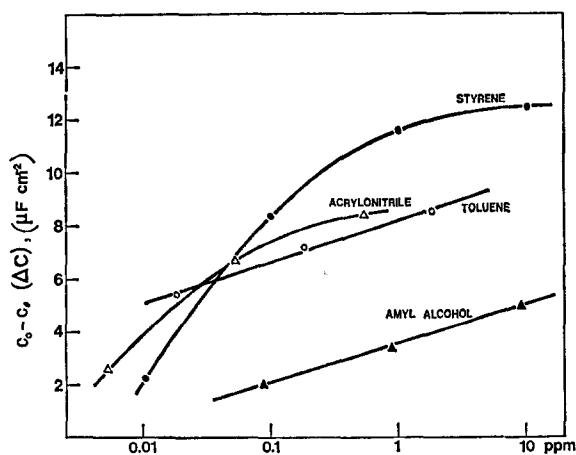| t(s)	1 M HClO$_4$ (pre-electrolysis)	1 M H$_3$PO$_4$ (no purification)	1 M H$_3$PO$_4$ (chemical purification)
5	—	—	—
15	—	2·2	—
30	—	8·0	—
45	—	10·8	1·2
60	—	12·2	1·6
90	2·0	15·9	2·8
120	2·5	20·0	5·0
180	5·3	25·5	6·4
300	8·0	36·4	8·8

Fig. 7. Isotherms (calibration curves) at 25°C for the adsorption of various organic substances on Pt from 1 M HClO₄ solutions.

sensitive to the total carbon content. Fig. 7 shows some calibration curves for organic substances. It can be seen that equal ΔC values are obtained for different concentrations of different substances. Practically, it will be the more surface active substance in a mixture which will be preferentially adsorbed. Thus it is necessary to bear in mind that with this method the purity of a solution is classified on the basis of the surface activity of its impurities. It is obvious that this concept of purity may not always coincide with the usual concept based on the value of the concentration of impurities. The most striking consequence of this is that in the presence of two substances with very different values for β, the electrode does not detect the substance with lower β even though its concentration may be much higher. This method is thus especially relevant to heterogeneous systems, but it may be useful in other cases as well. Thus the method is of course best used for the control of *high-purity* waters, (if the impurity content is very

high other analytical methods can be employed more profitably).

7. Some practical applications

7.1. Industrial water quality evaluation

As an example, three water samples (X, Y, Z) coming from the steam system of an industrial plant have been examined. The three samples were classified by means of a titrimetric analysis of CO_2 formed by combustion. Sample Z, coming from the boiler contained 5·2 p.p.m., while samples X and Y, coming from two different demineralization beds of the same plant, gave on analysis 2·5 and 3·0 p.p.m., respectively. Table 2 summarizes the values of the decrease in capacity (ΔC) measured at 0·4 V (RHE) with a Pt electrode. It is of interest to note that, as expected, ΔC increases as the impurity level increases. However, ΔC is clearly not linearly related to log carbon content and ΔC for sample X appears to be too low. This does not seem to be related to the presence of different kinds of impurities in the three samples. The intrinsic inaccuracy of the analytical technique used to evaluate chemically the carbon content is more likely to be the reason for the observed behaviour.

Fig. 8 shows the values of ΔC as a function of the carbon content varied by diluting progressively sample Z with 'blank' water. The relationship thus obtained is strictly linear and can be exploited as a calibration curve for the control of other water samples coming from the same demineralization bed. The scatter of the points shows that, in a relative sense, the accuracy of the measure is within 15–20%. In absolute terms the carbon content expressed in p.p.m. will obviously not be more accurate than the corresponding chemically determined value.

Table 2. *Characteristics of examined industrial water samples*

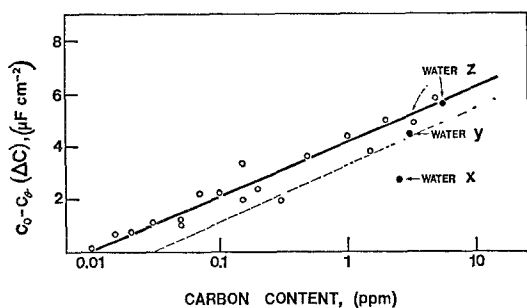| Type	Source	Carbon content (p.p.m.)	$\Delta C = (C_0 + C_\theta)$ ($\mu F\ cm^{-2}$)
X	Demineralized bed	2·5	2·8
Y	Demineralized bed	3·0	4·5
Z	Boiler	5·2	8·0

Fig. 8. Calibration curves obtained by diluting industrial water samples several times with ultra-pure water. (●) Original samples; (○) diluted samples. Experimental points to which the dashed line refer are not reported.

Conversely the technique does not provide absolute data if the pollution level cannot be measured by an independent technique.

Fig. 8 shows that the sensitivity can go down to 0·01 p.p.m. The dashed line indicates the ΔC versus log p.p.m. relationship obtained in the same way in the case of water Y. The horizontal shift can be attributed to an error in the 'chemical' value of the impurity level, as well as to a difference in the 'electrochemical' value related to impurities of different origin.

The scatter of experimental points about the solid straight line in Fig. 8 (namely the average accuracy of the measure) is unlikely to be due to the nature of the method, for the reproducibility within the same run is usually better

than 1%. The inaccuracy is more likely to depend on unsystematic errors, such as solution handling, C_o oscillation, dilution imprecision, etc. However, the accuracy is comparable to that of the other available methods [3] and it is to be emphasized that this degree of accuracy is retained by the present method at levels as low as 0·01 p.p.m.

7.2. Laboratory water quality evaluation

The best way to test the quality of laboratory water is to measure C or q_H as a function of time. We examined various water samples treated differently in order to improve their purity. Two alternative methods can be used to de-ionize water: distillation and demineralization by ion exchange. The latter method certainly gives better de-ionization as conductivity measurements can easily show [2]. However, organic pollution may be favoured by passing water through ion exchange beds. Fig. 9 shows that the slope of the linear C versus $t^{1/2}$ relationship is higher for de-ionized water than for distilled water. Similar conclusions have been reached indirectly by Raspi and Malatesta [40] in a study on silver electrocrystallization. Also, polarographic measurements by Stenina and Nikolaeva-Federovich [30] show a peculiar, deleterious effect brought about by de-ionized
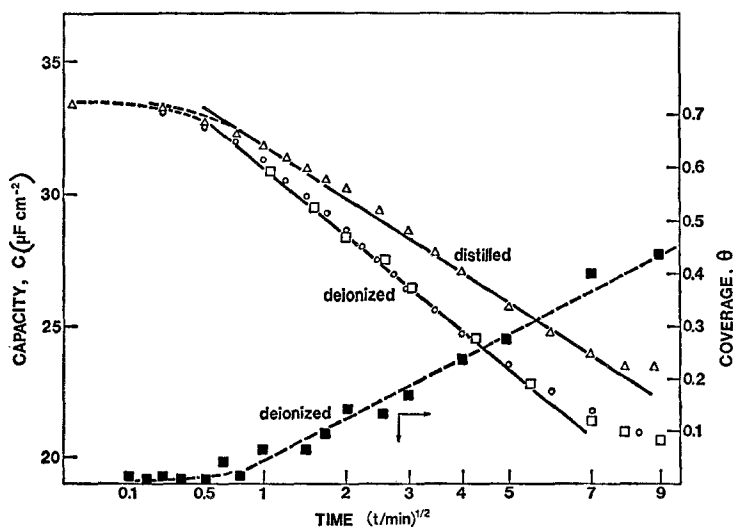

Fig. 9. Decrease in capacity and parallel increase in fraction of blocked surface sites with time for Pt in 1 M HClO$_4$ solutions made up with water from different sources. (○) De-ionized water used as such; (□) evaporated de-ionized water

water. However, distillation does not improve water purity as regards organic pollution. If de-ionized water is distilled, the purity of the product is the same as that of the feed water. The volatility of the impurities does not appear to be the primary reason for this. Fig. 9 shows that de-ionized water evaporated to half its initial volume still presents the same impurity level. From the above, we must necessarily conclude that distillation is ineffective in determining the background impurity level in water.

It is often reported in the literature that the dissolution of some permanganate and caustic potash in the intermediate stage of the still should be a powerful tool to remove organic impurities by oxidation. However, we could not obtain a detectable positive result. It may be that the permanganate is not effective in the working conditions of the still and at low impurity levels.

Further purification of distilled water is extremely important as regards the preparation of 'blanks'. Chemical purification with H_2O_2 has been found to be more effective. This reactant has the advantage that it is easy to eliminate. An example of its action has been shown above in Table 1 in the case of H_3PO_4 solutions. Fig. 10 stresses its effectiveness also in the case of plain water. Curve a refers to distilled water, while curve c refers to distilled water refluxed with H_2O_2. Although successful, the process is rather time-consuming.

Another method of removing organic pol-lution by oxidation is to distil the water through a heated column filled with CuO. Fig. 10 shows (curve b) that it is possible in this way to effect a small improvement.

Besides chemical methods, organic pollution can also be removed by an electrochemical technique, pre-electrolysis [41]. We tested two types of pre-electrolysis, inside and outside the cell, respectively. Outside-cell pre-electrolysis consists in storing up a large volume of water, to which the supporting electrolyte has been added, in a glass vessel equipped with two electrodes, a large anode and a small cathode. Organic impurities are removed by oxidation at the anode. Fig. 10 shows that the impurity reduction by pre-electrolysis depends on the electrolysis time. However, the atmosphere above the solution must be controlled with great care [42], and the transfer of solution to the cell inevitably requires some handling which can again reduce the purity of the solution.

Inside-cell pre-electrolysis [24] appears to be more effective, as shown in Fig. 11, inasmuch as two factors make this method more favourable in this case i.e. the absence of any subsequent handling and the higher anodic area/solution volume ratio.

The most effective technique to remove organic pollution is undoubtedly to filter the solutions through active charcoal which removes organic substances by adsorption. This method was introduced by Barker [43] and subsequently used by quite a number of workers [36, 39, 44–
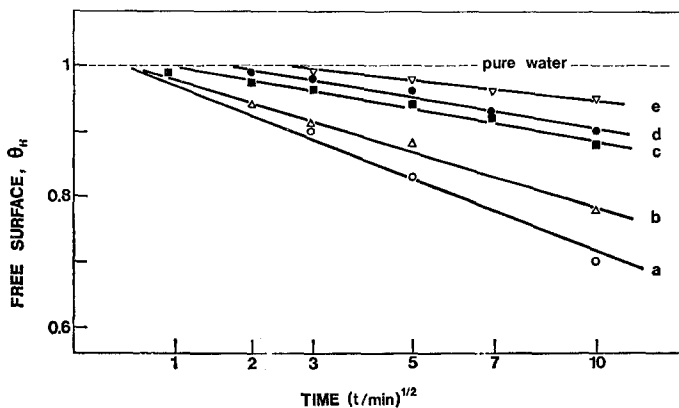

Fig. 10. Decrease in free surface sites with time for Pt in 1 M $HClO_4$ solutions made up with water differently treated. (a) Distillation; (b) distillation over heated CuO; (c) reflux with H_2O_2; (d) 2-days pre-electrolysis; (e) 8-days pre-electrolysis.
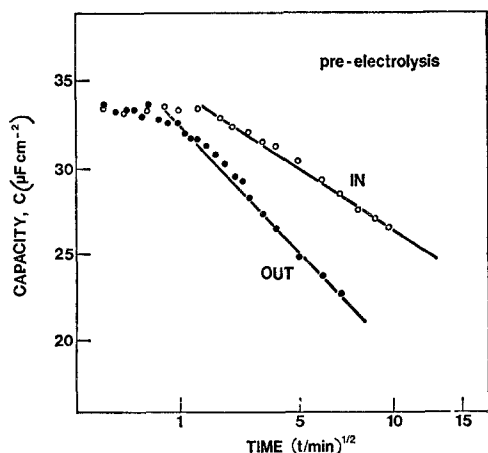
Fig. 11. Decrease in capacity with time for Pt in 1M $HClO_4$ solutions after pre-electrolysis inside (O) and outside (●) the cell.

47]. Under special conditions, the method can actually lead to ultra-pure water in which the capacity of an electrode remains constant over many days [36]. The present analytical technique evidences the effectiveness of the treatment with active charcoal. It can be seen in Fig. 12 that in the case of two waters of very different initial purity the greater improvement is observed in the water treated with active charcoal. However, this purification technique can be applied only

in particular cases. Nevertheless, a simple filtration through active charcoal ensures in any case a satisfactory improvement in purity [46].

8. Discussion

The results presented in this paper evidence the possibility of exploiting adsorption measurements for the estimation of pollution levels in water. A number of other electrochemical techniques have been proposed to the same end [32, 39, 46, 49–54]. The method suggested by Stenina and Nikolaeva-Fedorovich [39] is particularly interesting. These authors focused their attention on the problem of the purity of solutions used for electrochemical measurements. They observed a progressive decrease in the third-kind maximum of Cu^{2+} as the content of intentionally added camphor is increased. Their results show that the method is sensitive to below 0·01 p.p.m. Their 'blank' was water treated with active charcoal; a similar 'blank' would lead to a substantial improvement in the sensitivity of the method proposed here.

Techniques based on the measurement of double layer charging [39, 49, 52, 54] or of reaction rates [46, 49] do not have a general validity because they are especially sensitive to
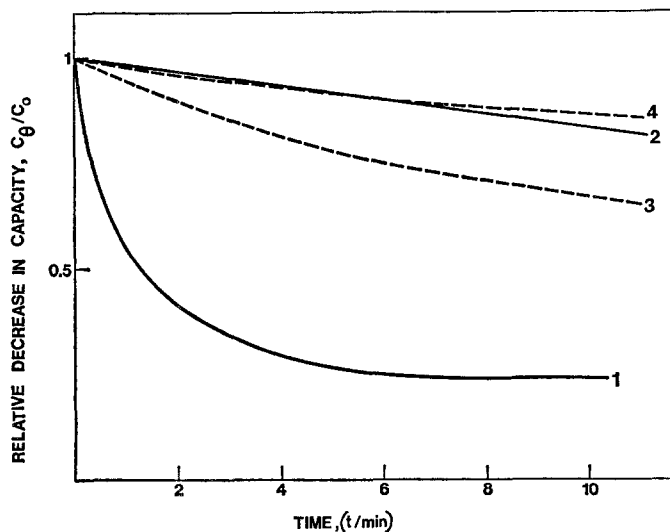

Fig. 12. Decrease in capacity with time for a Hg hanging drop electrode (———) and Pt electrode (– – – – – –) in solutions of surface inactive electrolytes treated in different ways. 1 and 2, original solutions; 3, filtration over active charcoal; 4, pre-electrolysis. Data for Hg taken from Reference [49].

ionized impurities. This remark applies particularly to surface potential measurements recently proposed [53] for non-ionized impurity detection. This limitation rules out all these techniques if the background ionic content changes from sample to sample. On the contrary, ionic impurities have much less effect on the response of the technique used in this paper. Cations have no practical influence even at relatively large concentrations due to their low adsorbability at the interface. Anions are more likely to be adsorbed and can be more surface-active. They can modify the capacity of the electrode [20], strongly in the case of Hg, less so in the case of Pt, so that a variable anionic content can produce a sensible oscillation in the value of C_o. However, q_H is much less influenced by anion adsorption [55]. The reasons for this are twofold. First, hydrogen adsorption occurs on Pt essentially at negative potentials with respect to the potential of zero charge [56]. In this region, anions are largely repelled by negative charges on the electrode surface. Second, ionic adsorption cannot give rise to large coverages because of strong particle–particle surface repulsion. From measurements on Pt it can be seen that ionic coverages above $0\cdot1$–$0\cdot2$ are seldom attained in the hydrogen adsorption region [55–57].

Ionic impurities can play an important role in the analysis of water. The practical cases discussed here refer always to de-ionized waters. More generally, in the case of domestic sewage and mixed industrial waters, the presence of ions appears to be unavoidable. The complexity of these systems makes it difficult to treat these waters by the present method. However, tap water can be treated, as ions, though present, are in comparatively small amounts. Cl^- is the most representative anion in tap water. If its concentration remains constant, ΔC is still indicative of organic pollution. Although studies especially focused on this aspect have not been made, qualitatively Cl^- can be said to decrease by itself the value of C_o in the case of Pt electrodes [58]. Thus the presence of Cl^- reduces the sensitivity, but not the applicability, of the present method. Actually, the general behaviour of Cl^- is much more complicated inasmuch as, depending on the value of the electrode potential the curve of C_o versus c_{Cl^-} may even show a maximum at about 5–10 p.p.m. Fe^{2+} ions, possibly present in this type of water, are much less interfering.

We have shown that these experimental techniques cannot be selective towards different organic substances. However, they are in fact extremely selective with respect to inorganic carbonaceous materials which are usually present as ions. These electrochemical techniques may thus present undoubted advantages with respect to the combustion method.

The range of applicability of the present method depends in principle on the nature of the electrode as well as of the impurities. On average, the lower limit appears to be about $0\cdot01$ p.p.m., while the upper limit is 10 to 100 p.p.m., if a Pt electrode is used. However, whereas the upper limit cannot be practically overcome because it is due to surface saturation phenomena, the lower limit can in principle be lowered inasmuch as the theoretical reference standard is represented by ideally pure water, i.e. water without any organic impurity.

The accuracy of these techniques is independent of the amount of solution to be analysed. In principle it may be possible to apply these techniques to microanalysis by employing smaller and smaller amounts of solution.

Acknowledgement

References

[1] M. Proskurnin and A. N. Frumkin, *Trans. Faraday Soc.*, **31** (1935) 110.
[2] R. C. Hughes, P. C. Müran and G. Gundersen, *Anal. Chem.*, **43** (1971) 691.
[3] R. B. Schaffer, C. E. Van Hall, G. N. McDermott, B. Barth, V. A. Stenger, S. J. Sebesta and S. H. Griggs, *J. Water Pollution Control Federation*, **37** (1965) 1545.
[4] C. E. Van Hall and V. A. Stenger, *Anal. Chem.*, **39** (1967) 503.
[5] A. W. Adamson, 'Physical Chemistry of Surfaces', 2nd ed., Interscience, New York (1967).
[6] B. B. Damaskin, O. A. Petrii and V. V. Batrakov, 'Adsorption of Organic Compounds on Electrodes,' Plenum Press, New York (1971).
[7] D. H. Everett, *Trans. Faraday Soc.*, **46** (1950) 942.

[8] R. Parsons, *Proc. Roy. Soc. London*, **261A** (1961) 79.

[9] R. Parsons, in 'Modern Aspects of Electrochemistry'. Ed. J. O'M. Bockris, Vol. 1, Butterworths, London (1954).

[10] G. Horanyi, J. Solt and F. Nagy, *J. Electroanal. Chem.*, **31** (1971) 87.

[11] L. Formaro and S. Trasatti, *Electrochim. Acta*, **15** (1970) 729.

[12] B. B. Damaskin and A. N. Frumkin, in 'Modern Aspects of Electrochemistry, Ed. J. O'M. Bockris, Vol. 3, Butterworths, London (1964).

[13] S. Trasatti, *Electrochim. Metall.*, **1** (1966) 267.

[14] G. J. Hills and R. Payne, *Trans. Faraday Soc.*, **61** (1965) 316.

[15] R. D. Armstrong, W. P. Race and H. R. Thirsk, *Electrochim. Acta*, **13** (1968) 215.

[16] J. S. Riney, G. M. Schmid and N. Hackerman, *Rev. Sci. Instr.*, **32** (1961) 588.

[17] D. R. Flinn, M. Rosen and S. Schuldiner, *Collect. Czech. Chem. Commun.*, **36** (1971) 454.

[18] S. Trasatti, *Electrochim. Metall.*, **2** (1967) 12.

[19] M. W. Breiter and S. Gilman, *J. Electrochem. Soc.*, **109** (1962) 622, 1099.

[20] P. Delahay, 'Double Layer and Electrode Kinetics', Interscience, New York (1965).

[21] M. W. Breiter, 'Electrochemical Processes in Fuel Cells', Springer-Verlag, Berlin (1969).

[22] S. Gilman, in 'Electroanalytical Chemistry', Ed. A. J. Bard, Vol. 2, Dekker, New York (1967) p. 111.

[23] A. Capon and R. Parsons, *J. Electroanal. Chem.*, **39** (1972) 275.

[24] L. Formaro and S. Trasatti, *Electrochim. Acta*, **12** (1967) 1457.

[25] L. Formaro and S. Trasatti, *Anal. Chem.*, **40** (1968) 1060.

[26] D. O. Hayward and B. M. W. Trapnell, 'Chemisorption', 2nd ed., Butterworths, London (1964).

[27] R. Parsons and F. G. R. Zobel, *Trans. Faraday Soc.*, **62** (1966) 3511.

[28] E. Dutkiewicz, J. D. Garnish and R. Parsons, *J. Electroanal. Chem.*, **16** (1968) 505.

[29] B. Damaskin, A. Frumkin and A. Chizhov, *J. Electroanal. Chem.*, **28** (1970) 93.

[30] S. Trasatti, *J. Electroanal. Chem.*, **28** (1970) 257.

[31] J. Weber, Yu B. Vasilev and V. S. Bagotskii, *Elektrokhimiya*, **2** (1966) 515.

[32] H. Jehring and W. Stolle, *Collect. Czech. Chem. Commun.*, **33** (1968) 1670.

[33] V. S. Bagotzky and Yu. B. Vassiliev, *Electrochim. Acta*, **11** (1966) 1439.

[34] G. Bianchi and P. Longhi, *Chim. Ind. Milan*, **46** (1964) 1280.

[35] G. Horanyi, D. Hegedüs and E. M. Rizmayer, *J. Electroanal. Chem.*, **40** (1972) 393.

[36] N. A. Hampson and D. Larkin, *J. Electroanal. Chem.*, **18** (1968) 401.

[37] A. M. Azzam, J. O'M. Bockris, B. E. Conway and H. Rosenberg, *Trans. Faraday Soc.*, **46** (1950) 918.

[38] S. Gilman, *Electrochim. Acta*, **9** (1964) 1025.

[39] E. V. Stenina and N. V. Nikolaeva-Fedorovich, *Elektrokhimiya*, **6** (1970) 1723.

[40] G. Raspi and F. Malatesta, *J. Electroanal. Chem.*, **27** (1970) 283.

[41] J. O'M. Bockris and A. K. M. S. Huq, *Proc. Roy. Soc. London*, **237A** (1957) 277.

[42] S. Schuldiner, B. J. Piersma and T. B. Warner, *J. Electrochem. Soc.*, **113** (1966) 573.

[43] G. C. Barker, 'Square Wave Polarography', Part 3, A.E.R.E., Harwell, England, C/R 1563 (1957).

[44] J. E. B. Randles, in 'Transactions of the Symposium on Electrode Processes', Ed. E. Yeager, Wiley, New York (1961), p. 366.

[45] K. M. Joshi, W. Mehl and R. Parsons, in 'Transactions of the Symposium on Electrode Processes', Ed. E. Yeager, Wiley, New York (1961), p. 249.

[46] S. D. James, *J. Electrochem. Soc.*, **114** (1967) 1113.

[47] D. A. Jenkins and C. J. Weedon, *J. Electroanal. Chem.*, **31** (1971) App. 13.

[48] T. Yoshida, T. Ohsaka and S. Nomoto, *Bull. Chem. Soc. Japan*, **45** (1972) 1585.

[49] B. Cosovc and M. Branika, *J. Electroanal. Chem.*, **46** (1973) 63.

[50] S. Schuldiner and M. Rosen, *J. Electroanal. Chem.*, **35** (1972) 1

[51] K. Linhart, *Tenside*, **9** (1972) 241.

[52] N. P. Berezina and N. V. Nikolaeva-Fedorovich, *Elektrokhimiya*, **3** (1967) 3.

[53] A. Faviani, M. Costa and S. Bordi, *J. Electroanal. Chem.*, **47** (1973) 143.

[54] B. Breyer and H. H. Bauer, 'Alternating Current Polarography and Tensammetry', Interscience, New York (1963).

[55] V. S. Bagotsky, Yu. B. Vaszilyev, J. Weber and J. N. Pirtskhalava, *J. Electroanal. Chem.*, **27** (1970) 31.

[56] S. Schuldiner and M. Rosen, *J. Electrochem. Soc.*, **118** (1971) 1138.

[57] Y. Chiu and N. A. Genshaw, *J. Phys. Chem.*, **73** (1969) 3571.

[58] M. W. Breiter *Electrochim. Acta*, **8** (1963) 925.