THE USE OF THE NUCLEAR MICROANALYSIS
OF LIGHT ELEMENTS IN ELECTROCHEMISTRY
APPLICATIONS TO ANODIC OXIDATION PROCESSES
BY DIRECT DETERMINATION OF ^{16}O AND BY ^{18}O TRACING

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The principles of the nuclear microanalysis of light elements in electrochemistry are described. Various applications to anodic oxidation processes in elemental analysis and by isotopic tracing are summarized.

Precise quantitative analysis of the constituents of thin films on the surface of solids is fundamental for the investigation of their formation mechanisms and for the understanding of their properties. Tracer experiments may give further insight in such phenomena as atomic transport, self diffusion and surface exchange with external media. Conventional analytical techniques often cannot be used for the determination of light elements near the surface of solids, especially when high sensitivity is required, as well as good depth resolution. Thus the electron probe integrates information on about the first micron of the sample and cannot distinguish between isotopes; its sensitivity for light elements is low. The ion probe may be most useful in many cases but its use for films thinner than some 100 Å is unreliable and the measurement of the total amount of an element per cm^2 is not precise. Both the electron and the ion probe yield results which depend on the matrix containing the analysed light elements; absolute calibration is most difficult and can, by no means, be universal. On the other hand the use of radioactive isotopes for tracer experiments is impossible for most of the light elements, owing to their very short life times.

In the frame of a programme devoted to the study of surface phenomena we developed a microanalytical method which consists of the direct observation of the nuclear reactions produced by charged particles bombarding the samples. The presence and amount of many light elements and of their stable isotopes may be determined·with this method with a very high sensitivity; universal absolute calibration is achieved and the location of the nuclei as a function of depth is possible with submicron resolution. In what follows we shall present the use of these methods to the determination or tracing of nuclei like D, ^{12}C, ^{14}N, ^{16}O, ^{18}O and ^{19}F and typical applications in the field of solid state electrochemistry, like anodic oxidation processes, corrosion and metal passivity.

THEORETICAL

Principles of Nuclear Microanalysis

These methods, first used in 1962, were described in detail in a number of publication[1−9]; only the basic principles will be described here succintly. Charged particles (p; d) in the 700 eV to 1500 eV energy range, from a low energy accelerator (typically a 2 MeV Van de Graaff) are directed on the sample; the beam diameter is typically 1 mm. The charged particles (p; α) produced by the nuclear reactions induced on the light nuclei located near the surface of the sample are detected by means of semiconductor detectors and their energy spectrum is analysed by conventional nuclear electronics. Well chosen Mylar films may stop the elastically back scattered incoming particles, providing practically background free detection. Nuclear reactions lead to monoenergetic particles and the resulting peaks in the energy spectrum are characteristic of the nuclei under study. Fig. 1 shows a typical spectrum so obtained. Interfering parasitic reactions may arise only from low Z substrata ($Z < 15$); a correct choice of the bombarding energy may minimise such effects.

The yield of the nuclear reactions depends only on the reaction cross-section and hence the matrix containing the nuclei has no influence on the results, provided that the nuclei are contained in a thin enough region near the sample surface. The quantitative analysis consists of comparing the counting rate from an unknown sample to that from a standard. The bombarding energy is chosen in the vicinity of a plateau of the cross-section curve. The results yield the total number of atoms per cm² near the surface of the sample. The analysis is non destructive. However adsorbed elements may be desorbed under vacuum or by the ionisation of the beam. This is a limitation of the method, shared by practically all other analytical techniques, except radiotracing.

Table I gives typical conditions for the analysis of some often measured nuclei as well as the corresponding counting rates for films containing 10^{16} atoms/cm². Let us recall that the relative
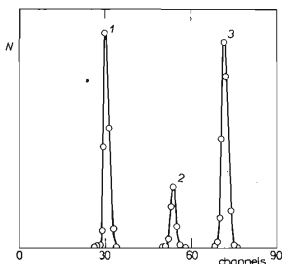

Fig. 1

Typical Proton Spectrum from (d, p) Reactions for an Anodic Oxide Film on Aluminium (1000 Å thick; natural abundance ^{18}O) Showing Separation of Proton Groups. Carbon Contamination of the Surface is Demonstrated

Target Al_2O_3; φ_{lab} 90°; $E_\alpha = 1\cdot06$ MeV; Mylar absorber 15 μ. 1 ^{16}O (dp), ^{17}O* with $E_p = 1\cdot4$ MeV; 2 ^{16}O (dp), ^{17}O* with $E_p = 2\cdot35$ MeV; 3 ^{12}C (dp), ^{13}C with $E_p = 3\cdot085$ MeV.

TABLE I

Typical Experimental Conditions for Nuclear Microanalysis

The counting rates may be multiplied by 3, using three identical detectors, when necessary.

Nucleus	^{16}O	^{18}O	^{14}N	^{19}F		^{12}C	D
Reaction	$^{16}O(d,p)^{17}O$	$^{18}O(p,\alpha)^{15}N$	$^{14}N(d,\alpha)^{12}C$	$^{19}F(p,\alpha)^{16}O$	$^{19}F(p,\alpha\gamma)^{16}O$	$^{12}C(d,p)^{13}C$	$D(d,p)T$
Bombarding energy keV	830	730	1 300	1 340[b]	870[b]	1 000	550
Energy of emitted particles, MeV	1·52	3·38	6·76	6·92	$\left.\begin{array}{l}7\cdot12\\6\cdot92\\6\cdot13\end{array}\right\}\gamma$	3·01	2·45
Thickness of Mylar absorber, μ	19	12	19	31	--	19	6
Counting rate[a]	1 600	4 600	470	315	4 200[c]	20 000	2 000

[a] For a film containing 10^{16} atoms/cm^2, a 1 µA beam per minute; the solid angle is 0·12 steradian at 150° detection angle; [b] for films of equivalent thickness <10 keV; [c] 3 in. × 3 in. NaI(Tl) scintillation detector at 7 cm.

statistical precision for N counts is $1/\sqrt{N}$, so that 10^4 counts should be accumulated for a 1% precision. Such a precision is usually achieved within some minutes of measurement time.

Concentration profiles may be determined by two methods. For depths of the order of some microns the energy spectrum of the emitted particles is analysed, yielding a concentration profile with a resolution of the order of 0·2 microns[3-6]. For profiles extending on some thousands of Angströms, the excitation curve of the nuclear reaction, *i.e.* its yield as a function of energy, is registered in the vicinity of a narrow resonance of the cross section. Here the profile may be calculated, with a depth resolution of the order of from 30 to 100 Å, depending on experimental conditions. A typical case is that of ^{18}O, in the vicinity of the 629 keV or 1 165 keV resonances of the $^{18}O(p,\alpha)^{15}N$ reaction[1-3].

It should be noticed that the elastic scattering of charged particles, and in particular of ^4He, allows to determine very small amounts of heavy nuclei near the surface of substrata of lower atomic mass. Some applications of such methods will also be given.

General Applications to thin Films and Electrochemistry

Elemental analysis includes those measurements which do not resort to tracing techniques. Here samples of natural isotopic composition are usually examined. The elements are determined

by measuring the isotope of the highest natural abundance: ^{16}O for oxygen (99·758%), ^{12}C for carbon (98·892%), ^{14}N for nitrogen (99·635%). As for hydrogen there is no reaction on ^{1}H, only deuteracted samples may be examined, using the D(d,p) T reaction.

A first domain of applications (using nuclear reaction or elastic scattering), consists in analysing the composition of thin films produced by various processes. In this way the stoechiometry of the films may be determined directly, when their qualitative composition is known. A typical case is that of films obtained by anodic oxidation of valve metals, which will be examined in more detail below. The applications may go far beyond the limits of electrochemistry proper and many be extended to processes like thermal oxidation, reactive sputtering, pyrolytic film deposition, epitaxial growth, *etc.* Let us quote the study of thermal oxides on silicon, and that of silicon nitrides[8,9]. On the other hand, as the electrolyte generally contains several elements, the question may arise, which are the elements contained in the film formed. Two typical cases may be quoted; the incorporation of anions from the electrolyte in anodic films[10,11] (see below) and the contamination of metallic films deposited by electrolysis. Thus a high chlorine content was detected by nuclear methods in electrolytically deposited gold films. More generally *trace analysis* may be achieved with very high sensitivity, for the nuclei of Table I, and in particular nitrogen and fluor.

A second application is the precise measurement of film thicknesses. In this case it is admitted that the stoechiometry of the film is well defined; hence the number of atoms per cm^2 of one of its constituents (oxygen for oxides) is a measure of the film thickness. This procedure allows to measure growth laws, kinetics, *etc.* with a very high precision, even for films thicknesses in the monomolecular range[12].

Such measurements may give a deep insight in phenomena like the passivity of metals. In this case ^{18}O enriched electrolytes are used to study the kinetics of oxygen fixation on the sample, althoug no tracing is needed, to minimise the effects of the oxidation of the samples once removed from the electrolyte, as the ambients have a very low isotopic ^{18}O content (0·204%).

The effects of surface treatments of samples may be evaluated in detail. Chemical and electrochemical polishing procedures may be studied, and the thickness of the oxide layer left on the sample measured with precision. Such methods were used to determine the optimal surface treatment of zirconium[14]. Recently these techniques allowed precise measurements of the traces of fluor and nitrogen which remain on tantalum after polishing in a mixture of sulphuric acid, nitric acid and fluoric acid; in particular some 10^{-2} μg/cm^2 of fluor was found on the samples. Among other applications let us quote: the close examination of electrodes after electrolytic treatment, a typical case is that of graphite anodes and the investigation of the anode effect the measurement of dissolution rates or last but not least the study of corrosion phenomena. Let us cite here the investigation of thermal oxidation of zirconium and of the heterodiffusion of oxygen in zirconium, which were carefully studied with these methods recently[5,15]. Applications to metallurgy are numerous[6].

Tracing with stable isotopes may be achieved for elements which have no long lived radioactive isotopes, using ^{18}O enriched products for oxygen and ^{15}N enriched products for nitrogen. Deuterium may be used with advantage, although tritium allows radiotracing of hydrogen: the isotope effects are smaller for deuterium and the ease of handling of stable isotopes is a non negligible advantage. The same applies to ^{13}C for carbon tracing, the analysis of which was not yet attempted.

The first application pertains to the determination of the origine of an element in a film formed by an electrochemical process. Thus when anodising various substrates in aqueous of organic solutions the question arises whether the oxygen in the film originates in the water, the solvent potassium nitrate or the salt. This may be elucidated using ^{18}O enriched water or salt for example); a recent work on anodic oxidation of silicon and tantalum in organic solvents was devoted to this subject[16].

Atomic transport during film formation (at high temperature or under high field) may be studied in detail using these techniques, as will be illustrated below for anodic oxidation.

Electrochemical exchange currents and self diffusion phenomena may be measured directly by observing the kinetics of isotopic exchange between a sample and a solution in various conditions. Such measurements simultaneously yield the exchange currents and the self diffusion coefficient in the substrate[10,17].

The very mechanism of electrochemical processes may be elucidated. Let us quote the case of the anodic oxidation of nickel hydroxide for which two mechanisms operate simultaneously, OH^- uptake and H^+ repulsion: the latter does not lead to ^{18}O uptake in a labelled bath and its proportion may thus be determined by tracing[17].

APPLICATIONS TO ANODIC OXIDATION PROCESSES

Elemental analysis. Faradic efficiency measurements and ion incorporation. The determination of the absolute number of oxygen atoms fixed per cm^2 on the sample surface, when correlated to coulometric measurements, allows to measure the mean charge balance per oxygen atom. When the electronic current is negligible (or well known, using a redox system for example), this allows to calculate the proportion of the oxygens fixed as O^{2-} and of those fixed as a polyatomic anion (SO_4^{2-}, NO_3^-, etc.)[11].

Direct measurement of incorporations. Once the amount of anionic incorporation is calculated, the incorporated element may be determined directly and its amount correlated to the oxygen content of the film, thus confirming the calculation[11]. Fig. 2 illustrates such a measurement for anodic films formed on tantalum in concentrated nitric acid; the oxygen nitrogen correlation fully confirmed the results of the coulometric measurements.
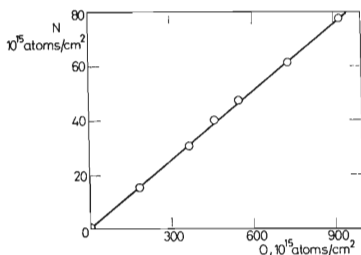
FIG. 2

Nitrogen Content as a Function of Oxygen Content for Films Formed on Tantalum in 93% HNO_3 at Various Current Densities $0.1\ mA/cm^2 < J_{ox} < 10\ mA/cm^2$

The precise measurement of the growth laws of anodic films for various fixed oxidation currents, J_{0x} as a function of the oxidation potential V_{0x} allows the determination of the field of formation E_{0x}, and of the overpotentials η at the metal-oxide and oxide-solution interfaces[12]. The influence of the initial layer of oxide on the sample surface on the growth mechanism may be demonstrated.

Other applications are precise dissolution rate measurements of anodic films, to characterise their chemical properties.
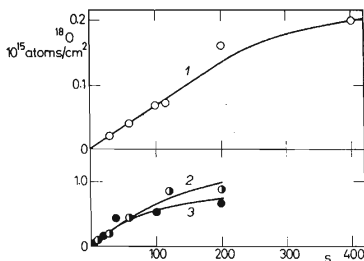

Fig. 3

Number of ^{18}O Atoms in Oxides Initially Formed at 20 Volts in ^{18}O Depleted Solution as Function of the Time of Exchange in an ^{18}O Enriched Solution

1 Polished tantalum; *2* unpolished aluminium; *3* polished aluminium. Number of ^{18}O atoms for the continuation of curve *1*:

Table II

Numerical Values of Fig. 3 for Long Time of Exchange on Ta_2O_5

Time, s	500	3 000	$2\cdot4 \cdot 10^4$	$6 \cdot 10^4$	$2\cdot4 \cdot 10^5$
^{18}O, 10^{15} atoms/cm^2	0·24	0·36	0·66	0·71	0·71

^{18}O Tracing

Transport mechanisms. In these experiments an oxide layer is formed in an ^{18}O enriched solution, and further oxidised in a natural solution. The quantity of the ^{18}O atoms after the second treatment and their location are then determined by the ^{18}O

(p, α) ^{15}N resonance method. In the case of aluminium[1] and of tantalum[10], in aqueous solution, both the quantity and order of the ^{18}O labelled atoms are conserved, indicating that oxygen is not moving or moves by a highly correlated vacancy mechanism. Porous oxidation of aluminium is presently studied with similar techniques.

Electrochemical exchange currents may be measured as shown above; an interesting case is when the self diffusion coefficient of oxygen in the oxide is negligible. In this case (Fig. 3 and Table II) the exchange properties of the first atomic layer are measured[12]. Here the oxide layer, prior to exchange, was grown in a ^{18}O depleeted solution (0.008% ^{18}O), to enhance precision. This result clearly illustrates the sensitivity of the method.

Field induced self diffusion effects may be studied, by forming first an oxide film in a natural solution and then maintaining it under its formation potential in an ^{18}O enriched solution. Such experiments on silicon showed that ^{18}O exchange is complete after 3 days for a 400 Å thick oxide film whereas no exchange occurs when no potential is applied[18,19].

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