

Use of Nuclear Techniques in the Characterization of Chrome Black Solar Absorber Surfaces

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Abstract

A set of electrodeposited chrome black solar absorbers has been subjected to ion beam analysis in an attempt to determine the concentration depth profiles of the major elemental constituents. Chromium distributions were obtained using the $^{52}\text{Cr}(p,\gamma)^{53}\text{Mn}$ nuclear reaction, which is resonant at $E_p = 1005.2$ keV. The possibility was investigated of inferring oxygen distributions from the γ -ray lineshapes (measured with a Ge(Li) detector) of the direct capture reaction $^{16}\text{O}(p,\gamma)^{17}\text{F}$. Concentration profiles were also obtained for fluorine and sodium contaminants in some chrome blacks. Complete experimental details are given of the various nuclear techniques used. The results of these measurements are discussed in terms of the microscopic physical features of the selective surfaces and are related to the known photothermal properties of the surfaces.

1. Introduction

One approach to efficient conversion of solar energy involves the use of selectively absorbing surfaces (Keyes 1972; Meinel and Meinel 1977). Ideally, such collector surfaces should be perfectly absorbing for solar wavelengths (i.e. up to $\sim 1.5\ \mu\text{m}$) and have minimum IR emittance (or, by Kirchhoff's law, an IR reflectance near to unity, because a black body spectrum has a significant intensity only at wavelengths greater than $1.5\ \mu\text{m}$ for all temperatures of practical interest in connection with photothermal conversion). Such properties are not normally found in a single material, and modern popular selective surfaces are in fact composites of thin films, that are transparent to IR and opaque to solar radiation, deposited on good thermally conducting polished metal substrates such as copper and aluminium (Mattox 1976).

The literature contains an increasing number of prescriptions for designing successful selective surfaces (Fan and Zavracky 1976; Craighead and Buhrman 1977; Fan and Spura 1977; Granqvist and Niklasson 1978; Window *et al.* 1978). One important category of selective surfaces is the cermet film, which is comprised of small metal particles embedded in a dielectric medium (Zeller and Kuse 1973; Craighead and Buhrman 1977). The most widely used cermet film surface is the chrome black coating (McDonald 1975; Driver *et al.* 1977), the composition of which is believed to involve amorphous or extremely fine grained chromium metal in an isolating Cr_2O_3 matrix (Fan and Spura 1977; Window *et al.* 1978). Although the suitability of using such blacks as efficient photothermal devices has been recognized for many years (Pfund 1933), their physical and optical properties are still not understood in detail.

Several groups have tried to identify the physical mechanisms which are responsible for the measured photothermal behaviour of selective surfaces, usually by searching for correlations between observed optical (e.g. absorptance, thermal emissivity) and physical (e.g. film thickness, surface topography, grain size distribution) properties (O'Neill *et al.* 1977; Ritchie and Window 1977; Granqvist and Niklasson 1978; Window *et al.* 1978). The conclusions of such studies are not always unambiguous, which is hardly surprising given the complex nature of the surfaces. For example, Window *et al.* (1978) found that the optical properties of chrome black coatings (in particular, their very high solar absorptance) were consistent with a graded chromium film adjacent to a dielectric layer on the substrate. They also found that the photothermal performance depended sensitively on the thickness of the dielectric layer. However, in a study of RF-sputtered $\text{Cr}_2\text{O}_3/\text{Cr}$ films, Fan and Spura (1977) suggested that analogous electroplated chrome blacks could be modelled by a cermet film composed of polycrystalline Cr_2O_3 and fine grained chromium metal, in which the front surface was almost entirely Cr_2O_3 and the metal concentration increased towards the coating-substrate interface.

Theoretical modelling studies have been inhibited by uncertainties in the chemical and structural composition of the thin film coatings. Because the films are so thin (usually $<0.5\ \mu\text{m}$) such information is difficult to obtain. The only chemical data available are derived from sputter-Auger measurements, which indicate a continuously varying chromium-oxygen composition (Sowell and Mattox 1976). Given this present lack of knowledge, it is imperative to develop analysis techniques for the quantitative determination of chromium and oxygen. Such information, in association with a complete characterization of the photothermal properties of the sample, should be extremely valuable in exposing the important parameters whose values need to be optimized for most efficient solar energy utilization.

The present paper describes an experimental study of a set of chrome black samples (supplied to us by Dr B. Window, University of Sydney) whose photothermal properties have recently been reported (Window *et al.* 1978). Each sample in the set differs with respect to electroplating time, and is thus presumably characterized by different film thickness and composition. The samples have been bombarded by accelerated ion beams, and their chemical compositions and depth variation of element abundances have been determined. Parts of the present study have been briefly reported elsewhere (Clark *et al.* 1979; Switkowski *et al.* 1979).

2. Physical Characterization

Details of the sample preparation technique have been given by Window *et al.* (1978). Basically the chrome black surfaces were prepared by electroplating from a chromium-containing bath (Sivaswamy *et al.* 1974) onto polished nickel-plated (nickel thickness $\approx 1\ \mu\text{m}$) copper sheets of 0.7 mm thickness. The samples were electroplated for time periods of 20, 40, 50, 55, 60 and 70 s, and are hereafter designated respectively by these deposition times. As noted by Window *et al.*, the samples plated for 20 and 40 s were specular, with interference colours typical of dielectric films; those plated for 50 and 55 s looked nonspecular and grey; while those plated for 60 s and longer were specular and black. The solar photothermal properties of these surfaces were found to be optimum for plating times near 70 s, where the thermal emittance is at its minimum and the solar absorptance exceeds 90%.

Fig. 1 shows scanning electron microscope (SEM) photographs of the samples taken at magnifications of 5000 and 1000. An evolution of surface features with plating time is evident. A fine grained surface is observed for sample 20. This begins to crack and craze in samples 40 and 50, producing a mosaic appearance. In sample 55, the islands (of dimension 5–10 μm) created by the crazing start to disappear. By sample 60, the process has almost been completed, and a fine grained material is building up on the sample again. This phase corresponds to a minimum in the thermal emittance of the film. Finally the fine grained material covers the whole surface in 70. Window *et al.* (1978) have established that the film thickness lies typically within the range 2000–5000 Å for these samples.

Fig. 2 is an SEM photograph taken at an acute glancing angle near 85° in order to obtain a clear impression of the detail of the scales which are characteristic of sample 55. From this view it is possible to deduce a thickness of ~ 2500 Å for the uppermost layer, which was built up over a plating time of $\lesssim 55$ s and subsequently decomposed to leave the desired chrome black surface. Fig. 2 clearly emphasizes that any interpretation of a measured depth distribution (especially for samples 50, 55 and 60) must allow for the gross surface roughness that is characteristic of these samples.

3. Chromium Determination

The use of resonant nuclear reactions to determine the concentration of certain elements as a function of depth in solid samples has been developed over the last decade as a result of increasing interest in properties of surfaces and in surface-related phenomena. Amongst the pioneering measurements is the work begun by Amsel and Samuel (1962) using resonances in the $^{18}\text{O}(\text{p}, \alpha)^{15}\text{N}$ and $^{27}\text{Al}(\text{p}, \gamma)^{28}\text{Si}$ reactions to study anodic oxidation. An extensive review of the literature has been made recently by Bird *et al.* (1974).

The applicability of the technique depends upon the existence of an isolated strongly excited resonance in a nuclear reaction involving an isotope of the element to be analysed. Inspection of the energy level scheme shown in Fig. 1 of Switkowski *et al.* (1979) suggests that the resonance in the $^{52}\text{Cr}(\text{p}, \gamma)^{53}\text{Mn}$ reaction at a proton bombarding energy of $E_p = 1005.2$ keV might be suitable. This reaction involves ^{52}Cr , the most abundant (83.8%) chromium isotope. Gamma-ray yield curves have been measured in the vicinity of the 1005.2 keV resonance by other investigators (Arnell 1961; Schulte *et al.* 1975). Their results indicate that, although there are five weak (p, γ) resonances within ± 100 keV of the 1005.2 keV resonance (at $E_p \approx 918, 929, 953, 987$ and 1025 keV), this resonance is about 10 times stronger than the neighbouring resonances, and so is well suited for quantitative depth profiling of surface chromium films. The width of this resonance has been measured to be < 100 eV (Switkowski *et al.* 1979), which is quite acceptable for profiling purposes.

Experimental Details

Chrome black samples, each $2 \times 1.5 \text{ cm}^2$, were mounted on a tantalum target ladder affixed to a Huntington UHV linear-rotary motion manipulator. A standardizing target of natural chromium, prepared by evaporating spectroscopic grade chromium onto a 0.25 mm thick gold backing, was also included. The target thickness was determined by conventional mass difference methods, and was found to be

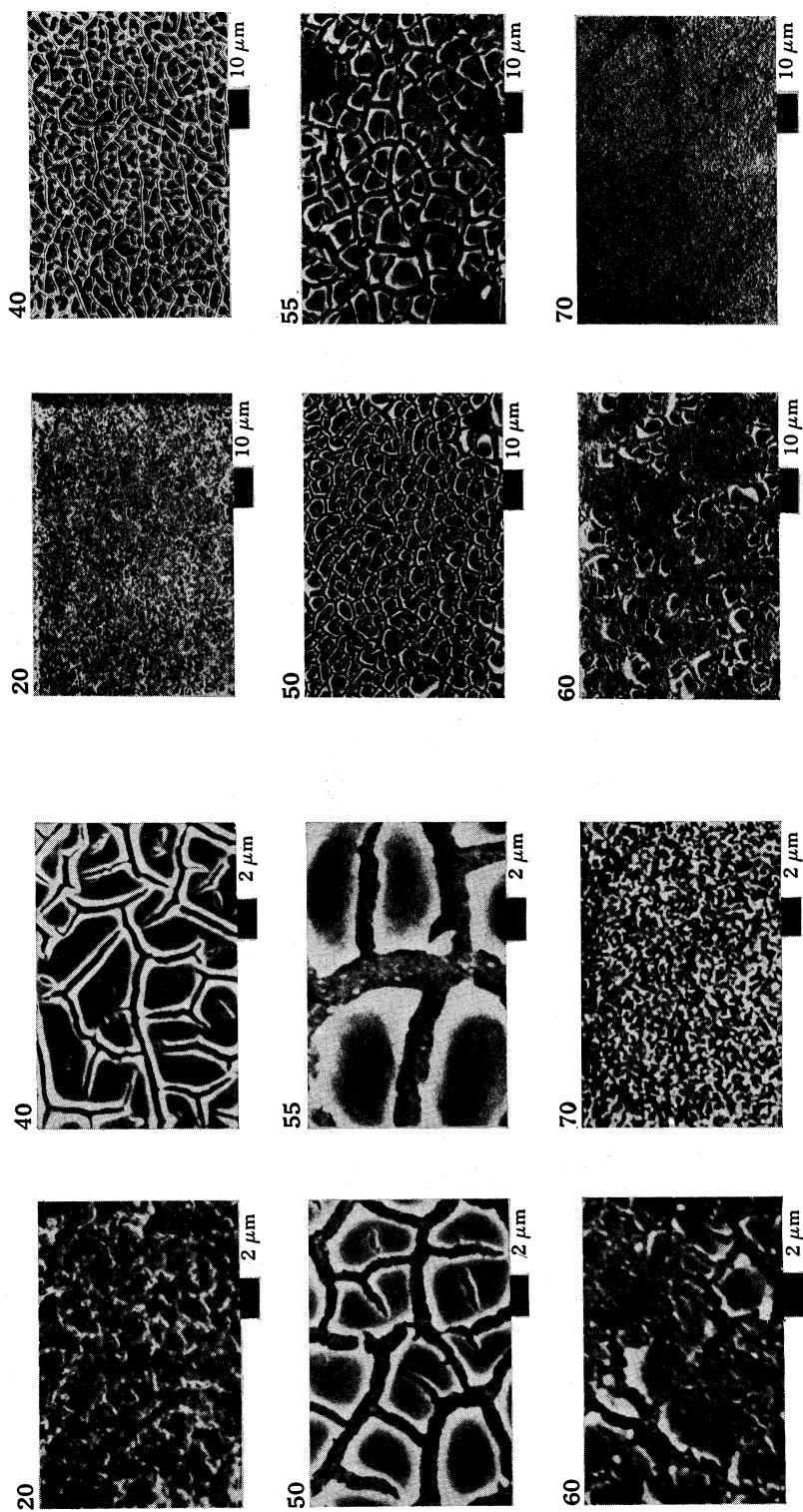


Fig. 1. SEM photographs of electroplated chrome black surfaces, labelled according to their plating times in seconds. A scale is provided by the indicated horizontal dimension of the black rectangle at the bottom of each photograph. Photographs to the left were taken at a magnification of 5000 and those to the right at a magnification of 1000. Sample 70 represents a good solar absorber surface.

$236 \pm 16 \mu\text{g cm}^{-2}$. The target holder was mounted in a stainless steel chamber, which was maintained at a pressure of 5×10^{-8} torr (7×10^{-6} Pa) by ion pumping.

Proton beams were delivered by the University of Melbourne 5U Pelletron accelerator, which directed them normally upon the target. The defocused beam was defined by an 8 mm diameter aperture, which was followed by an electron suppressor ring maintained at -500 V. The target chamber constituted a deep Faraday cup. Typical beam currents were $3 \mu\text{A}$.

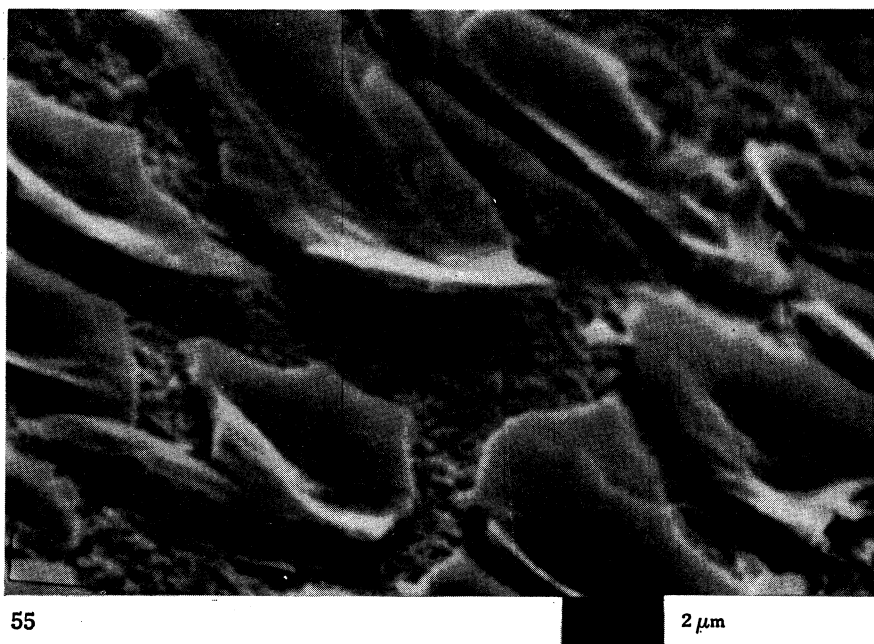


Fig. 2. SEM photograph of sample 55 for a glancing angle near 85° . The dual nature of the plated deposit is evident. The uppermost scaly layer has a thickness of $\sim 2500 \text{ \AA}$.

The γ -ray yield curves were measured by a 68 cm^3 Ge(Li) detector placed 2 cm from the target. Since the 1005.2 keV resonance populates a spin $1/2$ compound nucleus state (Maripuu 1970), the deexcitation γ rays have an isotropic angular distribution, and so the detector could be placed at 0° for convenience. The detector resolution was 2.3 keV for ^{60}Co γ rays, its photopeak efficiency for low energy γ rays having been measured with calibrated sources. Additional details have been given by Switkowski *et al.* (1978a, 1979).

Gamma-ray excitation functions were measured for each target over proton energies in the range from 1004 keV to (typically) 1040 keV in steps of 1 and 2 keV, usually for an integrated beam current of $300 \mu\text{C}$ per point. The 2048-channel energy spectra were analysed by a PDP-11/40 computer and stored on disc for subsequent analysis. Yield curves were generated for the 378 keV γ rays, which corresponded to the first excited state to ground state transition in ^{53}Mn . According to the decay scheme relevant to this resonance (Shulte *et al.* 1975), approximately 69% of all γ -ray cascades feed the first excited state.

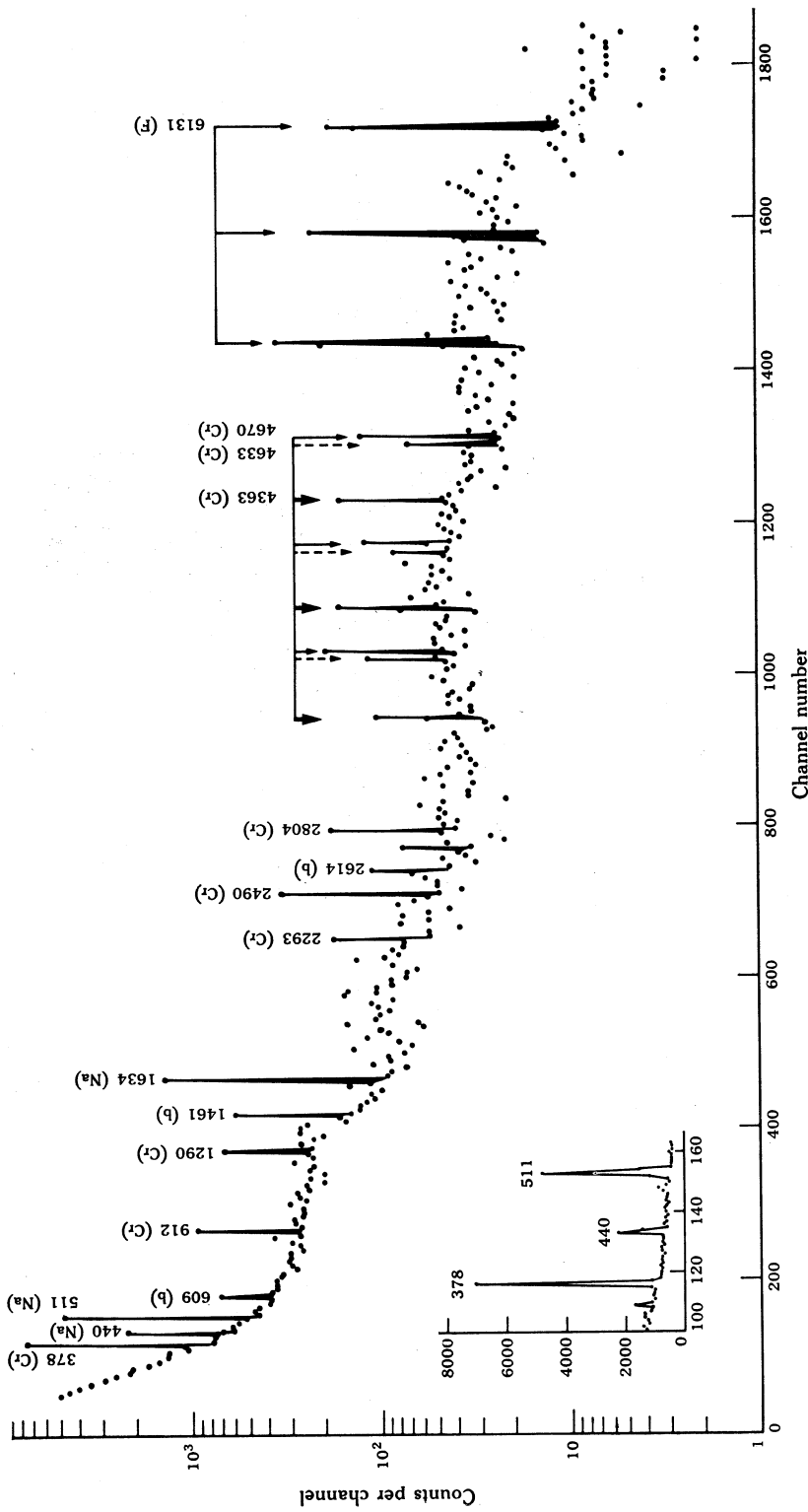


Fig. 3. Example of a γ -ray spectrum obtained for a 1.012 MeV proton beam incident on chrome black sample 70. Only every fifth channel is plotted except in the vicinity of a photopeak where the channel containing peak counts is also included. Gamma-ray photopeaks are labelled by their energies in keV and also either by the element (in brackets) which produced the γ ray upon interaction with protons or by the symbol b (in brackets) to refer to the room background. Groups of three arrows denote full energy and first and second escape peaks. The inset displays, in a linear plot, the γ -ray spectrum in the vicinity of the 378 keV photopeak.

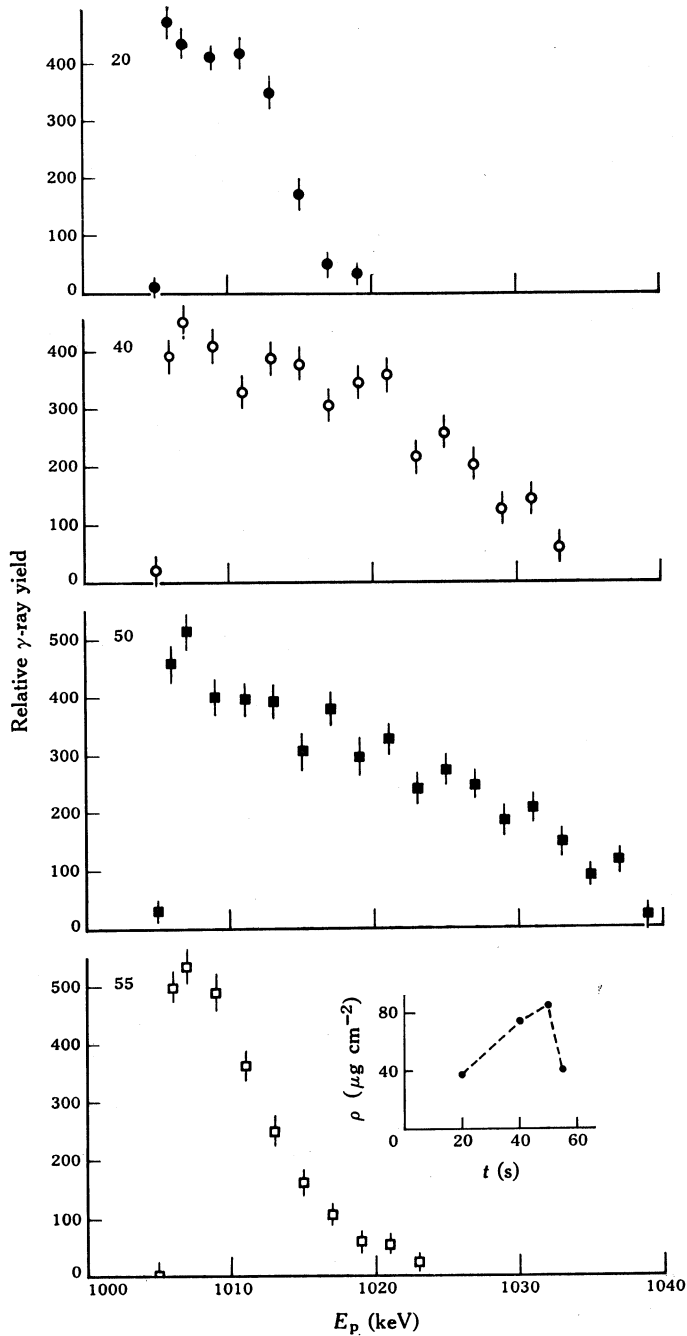


Fig. 4. Chromium depth distributions for four electroplated samples, showing the 378 keV photopeak yield per 300 μC of integrated proton current as a function of the proton energy E_p for the indicated chrome black surface samples. Error bars represent statistical uncertainties only. The inset displays the measured variations of the surface density ρ of chromium deposited versus the plating time t . The high energy tail of the γ -ray distribution for sample 20 is consistent with that expected for beam energy straggling. For samples 40, 50 and 55, the distributions reflect increasingly nonuniform chromium-containing surfaces. When the data of Figs 1 and 2 are considered, the most plausible interpretation of these profiles is that the electroplated samples develop very rough surfaces for increasing plating times up to 55 s.

Results

An example of a γ -ray spectrum obtained for sample 70 at $E_p = 1012$ keV is shown in Fig. 3. Several interesting features are evident, in particular, the strong signals from fluorine and sodium contamination within the target. The signature for fluorine is γ -ray emission from the $^{19}\text{F}(p, \alpha\gamma)^{16}\text{O}$ reaction, for which $E_\gamma = 6.13$ MeV is a key photopeak. The presence of sodium is indicated by the characteristic 440 keV γ -ray photopeak from $^{23}\text{Na}(p, p_1\gamma)$ reactions. These identifications were verified, and are discussed in Section 6. All other significant photopeaks seen in the spectrum arise from the $^{52}\text{Cr}(p, \gamma)$ reaction, and their relative strengths are qualitatively consistent with the branching ratios of Schulte *et al.* (1975). It should be noted that amongst the strongest peaks in the spectrum is the 378 keV photopeak and that this is clearly resolved from neighbouring lines.

One set of chromium profiles measured during the present study has been reported elsewhere (Clark *et al.* 1979). In Fig. 4 are shown additional profiles measured for sample areas adjacent to and 1 cm away from the first set. Absolute chromium abundances are obtained by comparing the integrated yield curve areas for the chrome blacks with that for the metallic thin film chromium standard (Gove 1959). The chromium areal densities obtained for the present set are approximately 15% lower than those measured by Clark *et al.*, owing to the spatial nonuniformity of the chrome black deposit, a feature noted previously by Window *et al.* (1978).

Comments

The chromium profiles of Fig. 4 and those given by Clark *et al.* (1979), together with the measured variation of chromium lay-down with plating time, point to the following evolution of the chrome black coating. For plating times up to ~ 50 s, the film thickness builds up linearly. The approximately equal plateau heights of the γ -ray yield curves for samples 20, 40 and 50 suggest that the average stoichiometry at the surface of these samples remains the same. A comparison of the plateau heights with that of the chromium standard produces an estimate of CrO_x , with $0.5 < x < 1.5$, for the chemical composition, assuming that oxygen is the only other major constituent and using the stopping power data of Ziegler and Andersen (1977). Such a comparison will be valid if the films, including the standard, provide uniform (i.e. continuous and of constant thickness) coverage of the substrate. Reference to Figs 1 and 2, however, shows that this may not be the case, so that any conclusions regarding chemical compositions must be regarded as tentative until independent oxygen determinations, such as described in the following section, are made.

For plating times between 50 and 55 s, the chromium content and film thickness decrease by a factor of about two. This mass loss of the electroplated film has been emphasized by Window *et al.* (1978). For a further increase in plating time, the thickness of the film builds up again and appears to become more chromium rich at the surface and also rougher (i.e. of nonuniform thickness), as evidenced by the high energy tails of the γ -ray yield curves of Clark *et al.* (1979). Because of this apparent roughness it is not possible to infer the chromium profiles with confidence. For the purpose of later comparison, the average surface composition of sample 70 appears to be $\text{CrO}_{0.35}$.

4. Oxygen Determination

While there are many nuclear techniques available for the quantitative determination of oxygen abundance, there remains considerable difficulty in obtaining accurate depth profile information. The $^{16}\text{O}(\text{d}, \text{p})^{17}\text{O}$ and $^{18}\text{O}(\text{p}, \alpha)^{15}\text{N}$ reactions have been used to this end in the past, but application of these reactions does not normally result in a surface depth resolution reasonably near that required for analysis of chrome black surfaces ($\sim 200 \text{ \AA}$). However, in an experimental program parallel to the present one, Scott and Russell (1978) have been exploring means for optimizing the use of $^{18}\text{O}(\text{p}, \alpha)^{15}\text{N}$, but as yet systematic data are unavailable.

A high resolution technique of considerable potential for oxygen profiling involves use of the direct capture $^{16}\text{O}(\text{p}, \gamma)^{17}\text{F}$ reaction. From the work of Rolfs (1973) it may be seen that, for proton beam energies less than 2.5 MeV, the (p, γ) cross section is a smoothly varying function of energy. As the primary γ ray has an energy which varies linearly with proton energy, a monoenergetic proton beam incident on a target having a uniform distribution of oxygen should produce a rectangular γ -ray lineshape with a width dependent on the target thickness and a resolution determined by the γ -ray detector. Although this technique was suggested in 1971 (Joy and Barnes 1971) few groups have pursued its application, presumably because the typical cross section for the reaction is only a few microbarns. We have undertaken an exploratory investigation with the chrome black sample 70 to determine the efficacy of this technique for oxygen profiling.

Experimental Details and Results

The results of Rolfs (1973) show that the cross section for the $^{16}\text{O}(\text{p}, \gamma_1)^{17}\text{F}$ reaction is greater than that for $^{16}\text{O}(\text{p}, \gamma_0)$ and that the γ_1 angular distribution peaks at 90° and has a minimum at 0° . Consequently the 68 cm^3 Ge(Li) detector was positioned at 90° and close to the target. All other details were similar to those for the chromium experiment. The choice of bombarding energy at which to perform the measurements turned out to be critical. Although the (p, γ_1) cross section increases (slowly) with energy for $E_p > 1 \text{ MeV}$, so also do the proton-induced reaction cross sections of the other abundant elements in the sample (Cr, Ni and Cu) and for them the energy variation is rapid because of the much larger Coulomb barriers involved. Examples of typical cross sections for these elements may be found in the literature (Woosley *et al.* 1975; Switkowski *et al.* 1978b; Zyskind *et al.* 1978). It was demonstrated experimentally that, at energies exceeding 1.3 MeV, the γ -ray yields from these elements (particularly Cu) were prohibitively large. A lower bound to the possible bombarding energy was established by studying an anodized tantalum target. It appeared that a statistically adequate γ -ray signal from ^{16}O could be obtained for a reasonable integrated bombarding current (to be defined below in this section) only for $E_p > 1.1 \text{ MeV}$.

Additional constraints on the bombarding energy were placed by the roles of reactions involving the contaminants: F and Na. An example of a γ -ray spectrum taken for a typical chrome black target at $E_p = 1.2 \text{ MeV}$ is shown in Fig. 5. The outstanding feature of the spectrum is the high yield from the $^{19}\text{F}(\text{p}, \alpha\gamma)^{16}\text{O}$ reaction, which is known to be strongly resonant in this bombarding energy region (Willard *et al.* 1952). So as to minimize the ^{19}F signal underlying the $^{16}\text{O}(\text{p}, \gamma_1)$ photpeak, an energy of 1.24 MeV was selected where the ^{19}F reaction did not have a resonance peak.

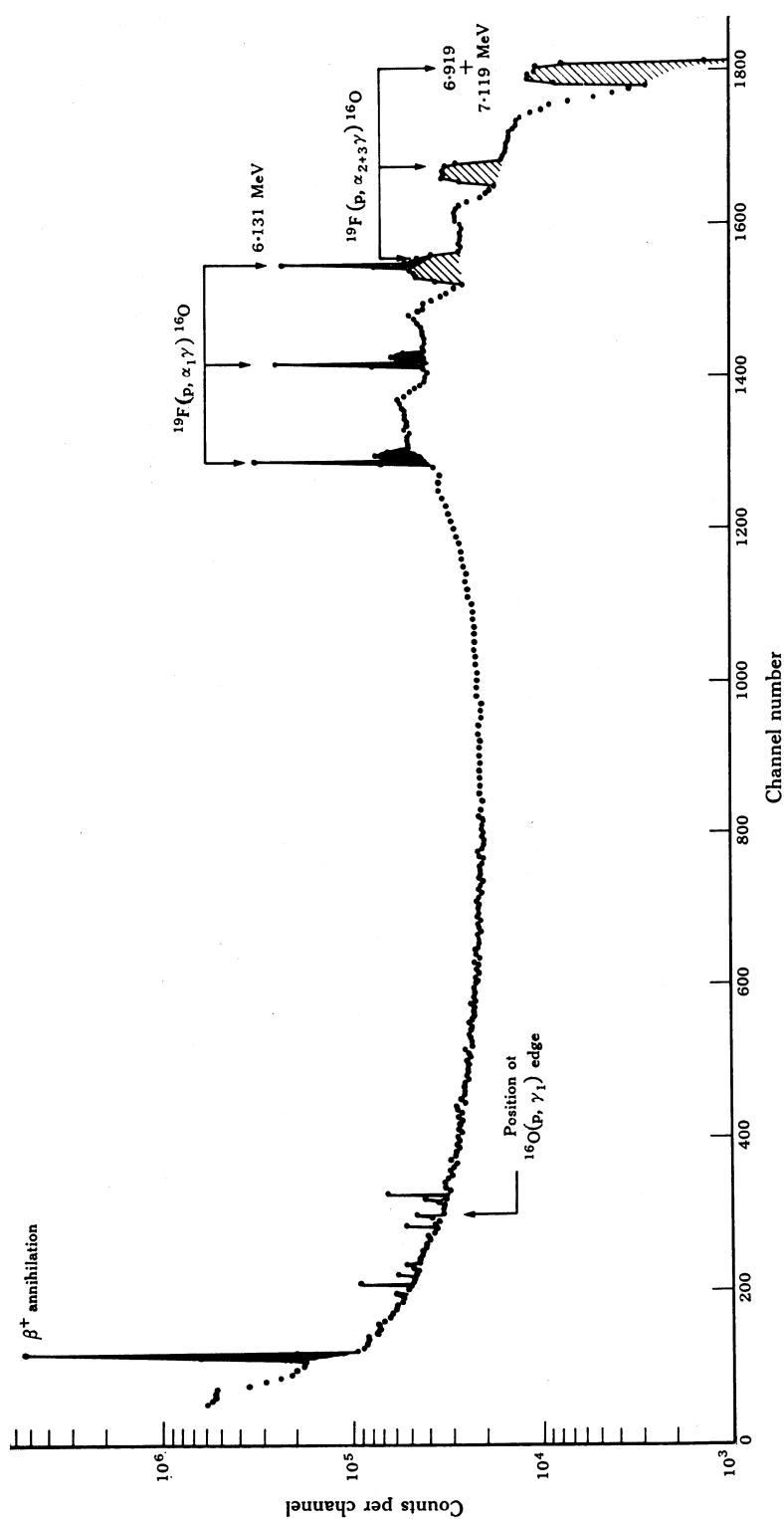


Fig. 5. Example of a γ -ray spectrum obtained for a 2.4 MeV molecular HH^+ beam (effectively, 1.2 MeV protons) bombarding sample 70. Only channels sufficient to illustrate the main features of the spectrum are plotted. Gamma-rays from $^{19}\text{F}(p, \alpha\gamma)^{16}\text{O}$ reactions are labelled. Groups of three arrows denote full energy and first and second escape peaks. For orientation, the calculated position of the $^{16}\text{O}(p, \gamma_1)$ lineshape edge is shown. At $E_p = 1.2$ MeV, there is no known strong (p, γ) resonance in chromium, nickel or copper.

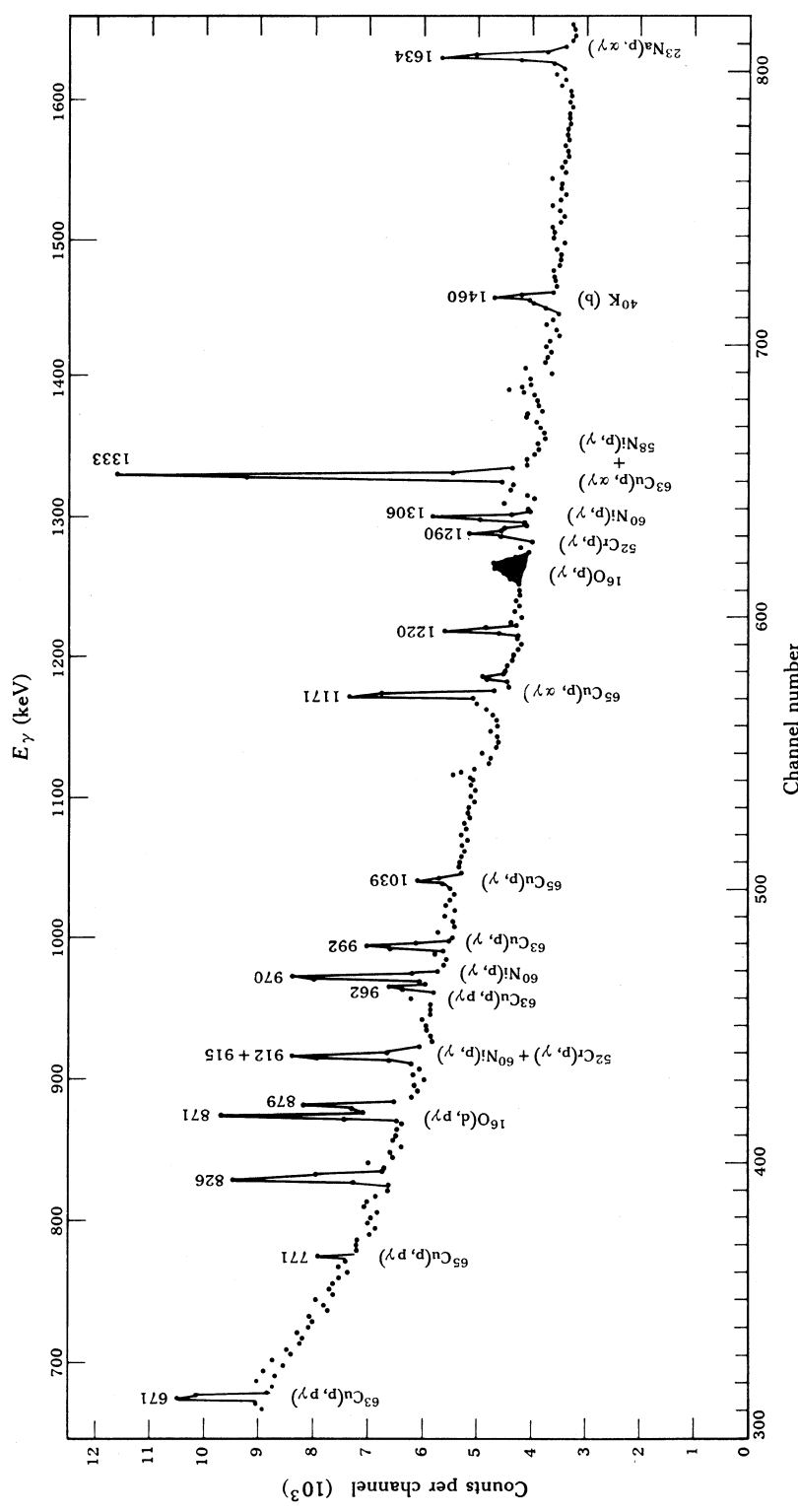


Fig. 6. Portion of a γ -ray spectrum for 2.48 MeV HH^+ irradiation of sample 70 (effectively, $E_p = 1.24$ MeV). Every second channel is plotted except in the vicinity of a photopeak where all channels are shown. Gamma-ray photopeaks are labelled by their energies in keV (refer to the upper E_γ axis) and also either by the pertinent nuclear reaction or by the symbol b (in brackets) to refer to the room background. The broad shaded peak is the $^{16}\text{O}(p, \gamma)$ profile of interest.

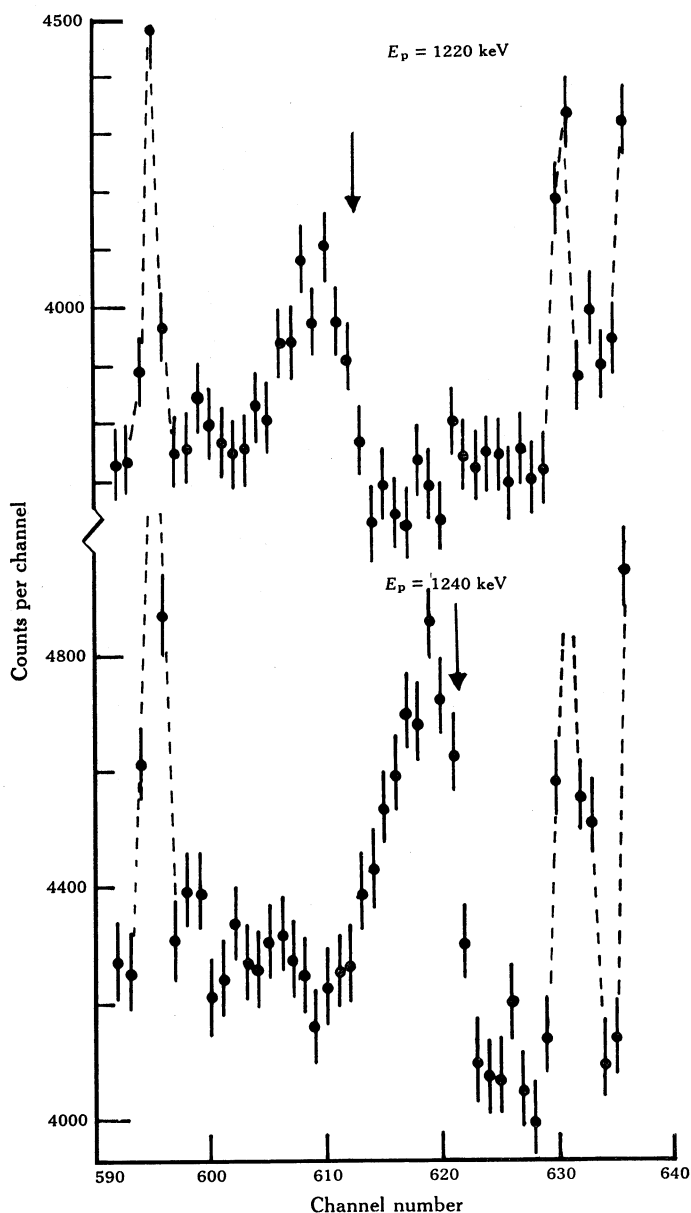


Fig. 7. Gamma-ray spectra for HH^+ bombardment of sample 70 expanded around the $^{16}\text{O}(\text{p}, \gamma_1)$ peak for the two indicated proton bombarding energies. Error bars represent statistical uncertainties, while the dashed lines are a guide to the eye. The calculated positions of the oxygen γ_1 edges are indicated by the arrows. The broad feature to the left of the arrows represents the oxygen depth profile in the target. The sharp peaks in the spectrum arise from (p, γ) reactions on other constituents of the target. The Ge(Li) detector resolution may be estimated from the observed width of these photopeaks. The calibration of the analyser is 1.96 keV per channel. The γ -ray spectrum at $E_p = 1220$ keV was acquired for 51 mC, and at $E_p = 1240$ for 92 mC integrated equivalent current of protons. Note the suppressed zero on the vertical scale.

In addition, the $^{23}\text{Na}(p, \alpha\gamma)^{20}\text{Ne}$ reaction (for which $E_\gamma = 1.634$ MeV) was not resonant at any depth within a typical chrome black film (Endt and van der Leun 1973).

An example of a γ -ray spectrum for sample 70 is shown in Fig. 6 for a proton energy of 1.24 MeV. The spectrum is characterized by a multiplicity of photopeaks superimposed upon a slowly varying background, most of which is due to the $^{19}\text{F}(p, \alpha\gamma)$ reactions. Most, but not all, photopeaks have been identified, but a complete identification would require a knowledge of the detailed composition of a target, such as may be obtained from a PIXE analysis. All oxygen data were obtained with a molecular HH^+ beam bombarding the target with typical currents of $\sim 5 \mu\text{A}$. It proved more convenient to operate the Pelletron accelerator in this mode rather than to run with protons, although the unresolved deuterium contamination of the molecular beam initiated a number of γ -ray producing reactions in the target.

In order to verify the identification of the $^{16}\text{O}(p, \gamma)$ peak, spectra were acquired at two bombarding energies of 1220 and 1240 keV, the relevant portions of which are shown in Fig. 7. One test of a direct capture γ ray is its energy variation with beam energy. This is evident in Fig. 7. The arrows indicate the calculated positions of the high energy γ -ray edges, using the measured gain and dispersion of the detection system, on the assumption that oxygen is distributed throughout the sample right up to its front surface. The reproducible positions of the discrete γ -ray photopeaks either side of the $^{16}\text{O}(p, \gamma_1)$ signal, which arise from bound state transitions in various compound nuclei, preclude the possibility of any gain changes affecting these measurements. The two spectra shown in Fig. 7, together with an additional measurement at $E_p = 1200$ keV, showed that the γ -ray spectrum background from reactions other than those involving ^{16}O was flat and featureless in the region of interest between channels 600 and 626 where the ^{16}O profiles for the chrome blacks were expected to fall. Such an accommodation on the part of the contaminant reactions was fortuitous.

A comparison of an oxygen profile extracted from the data shown in Fig. 7 with a chromium profile for sample 70 is made in Fig. 3 of Clark *et al.* (1979). Oxygen data are typically obtained in a 3 h run, with a complete depth profile being generated in one run at a single bombarding energy. For this comparison, differences between the chromium and oxygen runs in the detection system gains and the proton stopping powers have been accounted for. In order to convert energy loss to thickness, it is necessary to know the stoichiometry and density of the target. Such a determination was one aim of the present study. For illustrative purposes only, the depth scale of Clark *et al.* was deduced for an assumed average composition of $\text{CrO}_{0.4}$ (Switkowski *et al.* 1979) and a bulk density of 6.7 g cm^{-3} , intermediate between that of Cr and Cr_2O_3 . No correction was made for beam energy straggling in the targets.

It was intended to obtain absolute oxygen concentrations from a comparison of the (p, γ_1) yield with a standard anodized tantalum target of known oxygen content. However, for the target assembly used in the present study, the Ta_2O_5 target proved to be unstable to beam bombardment. Also an attempt to compare the 495 keV photopeak (this γ ray deexcites the first excited state of ^{17}F ; incidentally it has an isotropic angular distribution for which statistically significant yields could be obtained at considerably less integrated current) was frustrated by the presence in the chrome black spectra of a strong peak at 493 keV from the reaction $^{58}\text{Ni}(p, \gamma)^{59}\text{Cu}$ which could not be completely resolved from the 495 keV photopeak of interest. A

determination of the oxygen abundance was then performed using published absolute cross sections and angular distributions (Rolfs 1973) and measured Ge(Li) detector photopeak efficiencies. The average chemical composition of sample 70 was deduced to be CrO_x , where $x = 0.4 \pm 0.15$. Alternative techniques for determining absolute total oxygen concentrations more quickly and with higher precision are presently being explored.

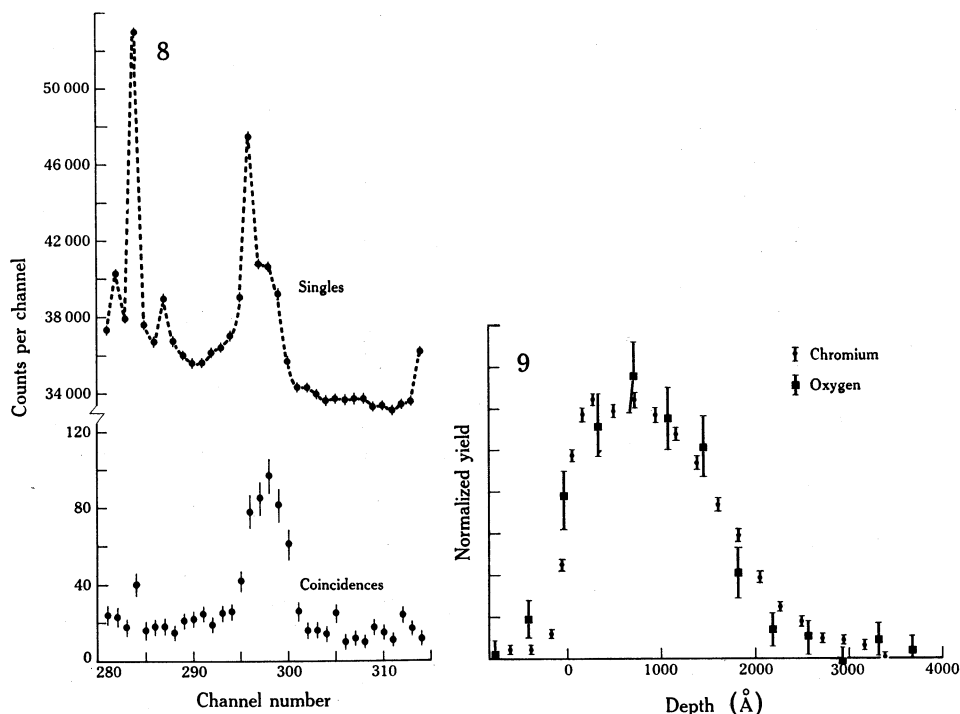


Fig. 8 (left). Gamma-ray spectra in the vicinity of the $^{16}\text{O}(\text{p}, \gamma)^{17}\text{F}$ peak. Error bars represent statistical uncertainties only, while the dashed line is a guide to the eye. Spectra were obtained for a 2.4 MeV molecular HH^+ beam (effectively, 1.2 MeV protons) and an integrated proton current of 320 mC, with a Ge(Li) detector operating in the singles mode and two Ge(Li) detectors operating in the coincidence mode as indicated (see text). Note the suppressed zero for the singles spectra (the sharp peak at about channel 284 in this spectrum arises from a 'contaminant' γ ray; see also Figs 6 and 7). The angle between the target and normal beam direction was 36° .

Fig. 9 (right). Comparison between the chromium and oxygen distributions in chrome black surface sample 70. The oxygen profile was determined by a Ge(Li)–Ge(Li) coincidence technique, and its average height has been normalized to that of the chromium profile in order to facilitate comparison. Error bars reflect statistical uncertainties only. The zeros of the depth scales are absolute and have not been normalized. The depth scale is appropriate to a uniform thin film of average composition $\text{CrO}_{0.4}$ with a bulk density of 6.7 g cm^{-3} . The depth resolution is determined by incident beam energy spread, straggling in the target and surface inhomogeneity. Additionally, for the oxygen determination, the detector resolution and Doppler broadening contribute to limit the resolution.

It is evident from Clark *et al.* (1979) that the chromium and oxygen depth distributions in sample 70 are the same within the uncertainties of the data. It seems that the long tails of the distributions shown in Fig. 4 are largely the result of variations of film thickness rather than variations in average composition. This is consistent with the rough nature of the chrome black surface observed with the SEM.

5. Coincidence Measurements

Joy and Barnes (1971) have pointed to the possibility of performing oxygen analyses using a coincidence technique to reduce background interference, noting that the primary γ ray from $^{16}\text{O}(\text{p}, \gamma_1)$ is in coincidence with an isotropic 495 keV γ ray. To this end we added a 60 cm^3 Ge(Li) detector to our experimental set-up so that a two detector configuration in the $\pm 90^\circ$ position resulted. Gamma rays which produced a signal in the smaller detector in the energy range 490–500 keV opened a coincidence gate via conventional circuitry, permitting the opposite detector to record a spectrum. A comparison of a singles and coincidence spectrum is shown in Fig. 8. For this run the target was inclined through an angle of 36° to the beam.

Clearly the signal-to-noise ratio has been much improved in the coincidence spectrum, but at the expense of the count rate. The running time necessary to acquire adequate statistics was ~ 10 h. For molecular beam currents of $5\text{ }\mu\text{A}$ on target, the count rate in the detectors was 5 kHz. While with proper target cooling it might have been possible to increase the beam current, the ensuing high count rates would have necessitated use of pile-up rejection—a sophistication, rendering application of this technique of oxygen determination less attractive for routine work. Attempts to use an NaI(Tl) detector to provide the gating pulse gave unsatisfactory results due to interference from the strong unresolved 511 keV annihilation radiation. An oxygen profile determined from the coincidence work and normalized to the measured chromium profile is shown in Fig. 9. This comparison is completely consistent with the oxygen profile measured in singles mode, which was described in Section 4.

6. Sodium and Fluorine Measurements

It proved straightforward to obtain depth profiles of sodium in the chrome black targets by observing the 1.634 MeV γ ray from the $^{23}\text{Na}(\text{p}, \alpha\gamma)^{20}\text{Ne}$ reaction, which is resonant at $E_p = 1010.5\text{ keV}$ (Endt and van der Leun 1973). There is no strong neighbouring $(\text{p}, \alpha\gamma)$ resonance which could confuse such an analysis. The 1.634 MeV γ ray was clearly evident in most spectra examined during the present study. As the $^{23}\text{Na}(\text{p}, \alpha\gamma)$ resonance energy is very close to the $^{52}\text{Cr}(\text{p}, \gamma)$ resonance energy, these data were acquired simultaneously with the chromium profiles. Comparison of sodium and chromium profiles indicated that the sodium is contained and distributed within the electroplated layer. No special significance is attached to the details of the sodium distribution profile; presumably the sodium originates from sodium hydroxide, which is included in the electroplating bath solution (Window *et al.* 1978).

It may be of interest to know the absolute sodium concentration within the chrome black. This was calculated from the published resonance strength (Endt and van der Leun 1973) for the 1010.5 keV $^{23}\text{Na}(\text{p}, \alpha\gamma)$ resonance of 55 eV and from the measured integrated 1.634 MeV γ -ray yield. Details of the calculation are given by Switkowski *et al.* (1975, 1978a). We have assumed that any γ -ray angular distribution effects have been effectively averaged out by our large solid angle detector. It was found that the abundance of atoms expressed as a ratio was typically $[\text{Na}]/[\text{Cr}] \approx 0.1$, a rather high value. It would be interesting to pursue the question of whether the presence of the sodium has a perceptible effect on the photothermal properties of electroplated chrome blacks.

Finally, in Fig. 10, we show a comparison of chromium, sodium and fluorine concentration profiles for a typical chrome black sample. Fluorine was profiled in the conventional way with the $^{19}\text{F}(\text{p}, \alpha\gamma)^{16}\text{O}$ reaction, which is resonant at $E_p = 874$ keV (Bird *et al.* 1974). As with sodium, the fluorine probably originates from H_2SiF_6 , a component of the electroplating bath.

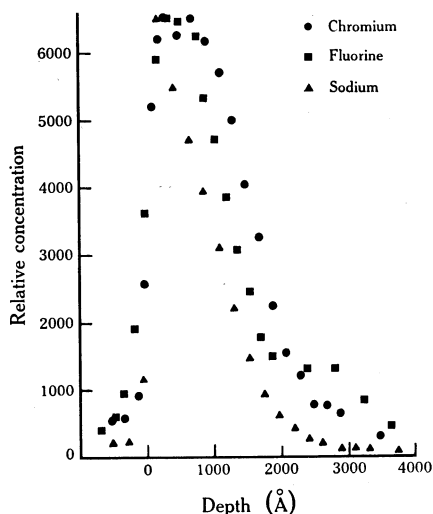


Fig. 10. Depth distribution of chromium, fluorine and sodium in chrome black surface sample 70. The depth scale is approximate and assumes a bulk composition of $\text{CrO}_{0.4}$. Elemental depth profiles are only relative and have been normalized to the same maximum yield for clarity.

7. Conclusions

We have investigated a variety of nuclear reaction techniques as probes of chromium, oxygen, fluorine and sodium in electroplated chrome black solar absorber surfaces. The efficacy of the $^{52}\text{Cr}(\text{p}, \gamma)^{53}\text{Mn}$ reaction (resonant at $E_p = 1005.2$ keV) has been demonstrated for chromium depth profiling. The measured variation with plating time of chromium concentration and distribution was found to be completely consistent with the physical measurements of Window *et al.* (1978) and with the recent α -particle backscattering data of Clapp *et al.* (1978). The detailed interpretation of the distributions must be guided by optical and/or electron micrographic inspection of the target surfaces, especially when these are rough.

The measured chromium profiles in themselves may suggest an average chemical composition of the electroplated film when the identities of other major elements present are known. This feature was tested on sample 70, for which the chromium profile data together with published stopping powers implied an average composition of $\text{CrO}_{0.35}$. The direct capture $^{16}\text{O}(\text{p}, \gamma)$ reaction was studied as a means of obtaining information on oxygen concentration for sample 70. Application of this technique was not straightforward owing to the low γ -ray yield from the reaction of interest and the strong signals from contaminant reactions. However, for a proton energy near 1.24 MeV, an oxygen distribution was obtained whose shape was consistent with the chromium profile and which indicated a bulk composition of $\text{CrO}_{0.4 \pm 0.15}$, in agreement with the value implied by the semithick target yield curve obtained with $^{52}\text{Cr}(\text{p}, \gamma)$. The precision of the oxygen determination could be significantly improved by use of comparison measurements against standard oxygen-containing targets.

Alternative techniques for more-rapid measurements of oxygen are presently being explored in the University of Melbourne laboratory. Application of the $^{16}\text{O}(\text{p}, \gamma)$ reaction technique to a systematic study of a variety of oxygen-containing solar absorber surfaces may prove tedious owing to the very low γ -ray yield.

Finally, fluorine and sodium contaminants in the surfaces have been observed with resonant nuclear reactions. Surprisingly, the measured sodium content in the chrome blacks was quite high and may significantly affect the stoichiometry of the surface and, correspondingly, its photothermal properties. As there may be other major contaminants in these surfaces to which the present techniques are insensitive, it would be useful to undertake a comprehensive measurement (using PIXE, for example) in order to identify the main elemental components of these plated chrome blacks.

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