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Quantitative PIXE analysis of impurities and their influence on the electrical properties of metal-free phthalocyanine

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The impurity content of commercial metal-free phthalocyanine (H_2Pc) powder has been determined by proton-induced X-ray emission (PIXE), and high concentrations of some elements, including highly conducting iodine, were found. The effects on the impurity concentrations of heating the H_2Pc to 400° C for 1, 2, 3 and 4 h were investigated. This purification procedure leads to smaller although not negligible impurity content. Some electrical properties of H_2Pc were also measured as a function of purification time and it is shown that they are, as expected, greatly dependent on the impurity content.

1. Introduction

Organic semiconductors such as metal-free phthalocyanine (H_2Pc) are known to strongly absorb visible light and as such are very interesting compounds for use in photovoltaic [1–8] and photoelectrochemical cells [9–11]. However, the nature and the amount of various undesirable impurities in commercially available H_2Pc have not previously been clearly identified, and thus the processes required for purification are somewhat unclear [12, 13]. Two of us, using neutron activation analysis (NAA) and X-ray diffraction [14], have recently identified and measured the concentrations of some impurities in metal-free H_2Pc, copper phthalocyanine (CuPc) and iron phthalocyanine (FePc). Furthermore, inconsistent results on the electrical characteristics of H_2Pc have been reported [10, 11, 15] and are probably due to the differing concentrations of impurities present in the H_2Pc samples. One objective of this paper is to definitely show that some electrical properties of H_2Pc (especially d.c. conductivity and tan δ) are dependent on its impurity content.

Another of our objectives was to demonstrate that proton-induced X-ray emission (PIXE) is a good analytical technique to estimate the impurity content in semiconducting solids. For that purpose, we have measured the impurity content in commercially available H_2Pc and in samples submitted to various heat treatments. The d.c. conductivity and dielectric losses were measured after each treatment and a correlation between them and the impurity content has been attempted.

2. Experimental set-up and procedures

The detection of the characteristic X-rays emitted when a target is bombarded with electrons (SEM), X-rays (X-ray fluorimetry), or charged particles (PIXE) [16] are well-established techniques for elemental analysis. The combination of the excitation of X-rays by protons, or other charged particles, and their detection with an Si(Li) detector constitutes a rapid method of multi-element analysis with sensitivity down to the p.p.m. level [16]. Three major advantages of PIXE are that only milligram quantities of sample are required, that each measurement takes only a short time (typically between a few minutes and half an hour), and that it is relatively inexpensive, given that an accelerator is available. It is therefore ideally suited to the rapid survey or monitoring of many samples [17]. Other advantages are the minimal sample preparation required, the good sensitivity, and the absolute concentrations that can be obtained, once the apparatus is calibrated. The advantage of PIXE for such measurements is that a wide range of impurity elements can be detected and that the data can be analysed on-line using modern computer programs [18].

A detailed description of the apparatus appears elsewhere [19, 20], so only the main features of our PIXE set-up will be mentioned. The University of Montreal EN1 Tandem accelerator provides a variable-energy proton beam of up to 100 nA on the target in the PIXE chamber, which is shown in Fig. 1. The proton beam is collimated to 3 mm diameter by a series of slits and then strikes the target at normal

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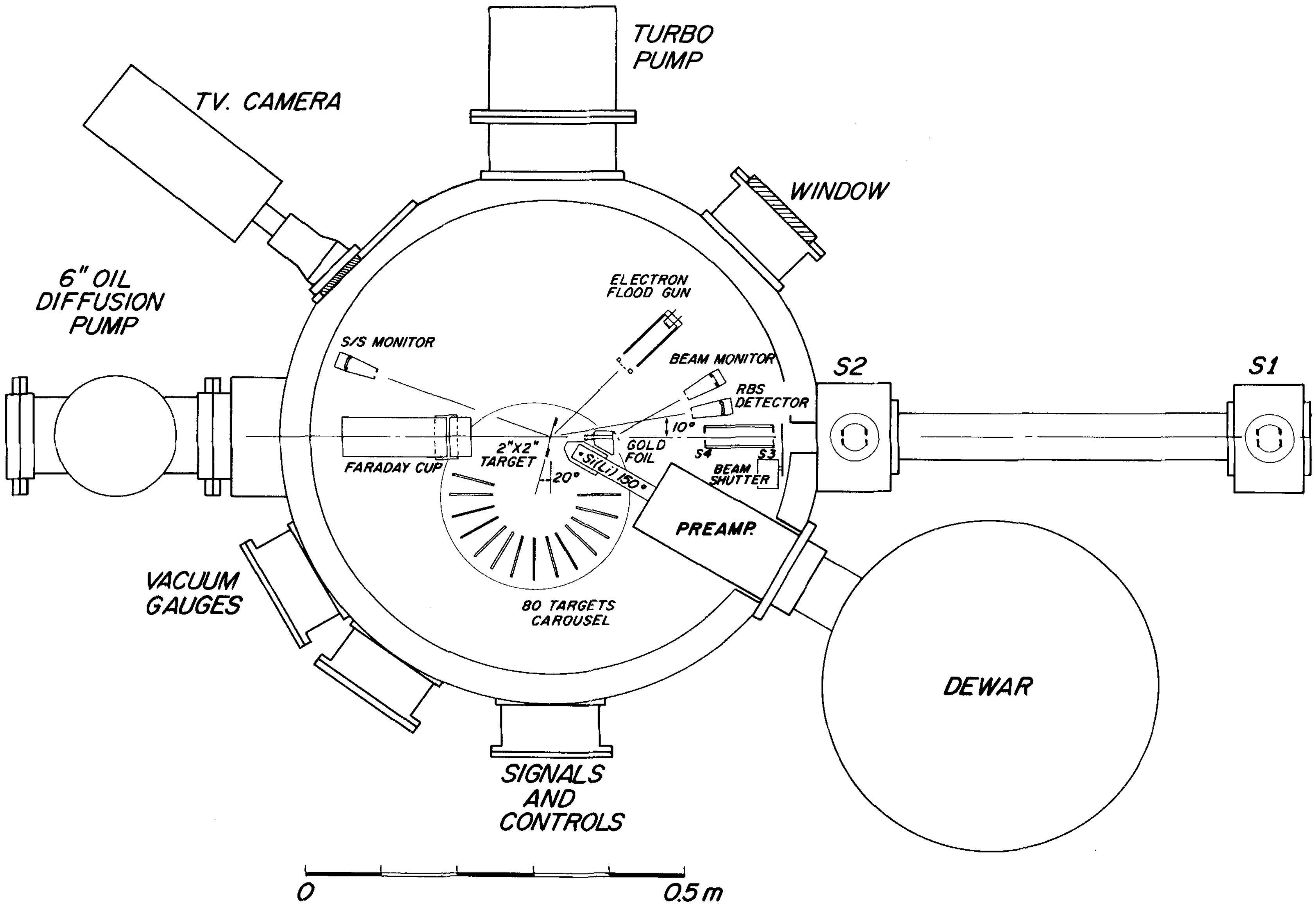

Figure 1 Diagram of the PIXE scattering chamber showing the beam collimators, the Faraday cup, the target carousel (replaced by a vertical target ladder for these measurements), the Si(Li) X-ray spectrome the RBS surface barrier particle detector at 170°, and the beam-monitoring detector. 1″ = 25.4 mm.

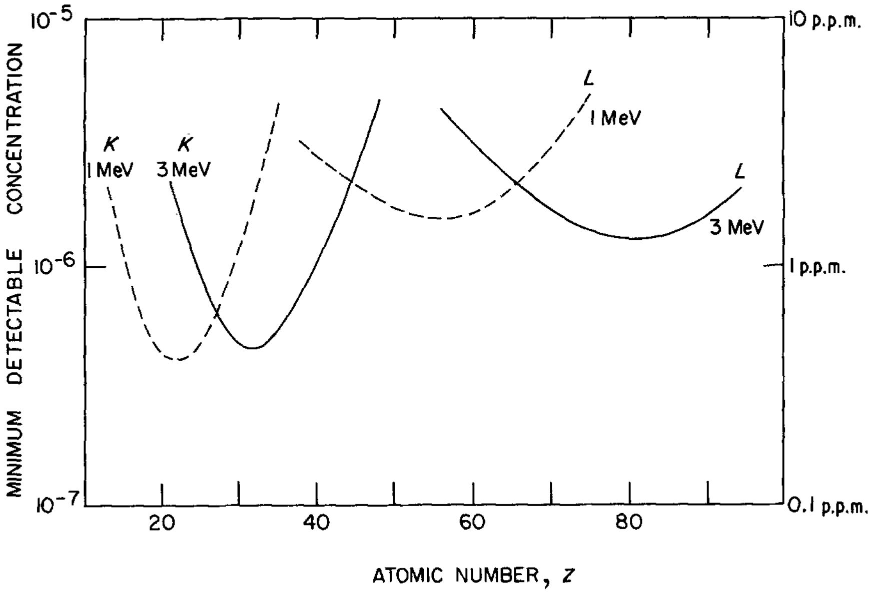

Figure 2 The thin-target sensitivity of PIXE as a function of the atomic number of the target element for proton energies of 1.0 and 3.0 Mev (after Johansson and Johansson [16]).

incidence. An electrostatic on-demand beam-pulsing system is used to reduce pulse pile-up in the detector electronics, and thus allows counting rates up to 3000 Hz to be used. The beam current on the target is continuously monitored by measuring the protons scattered at 150° by $10\,\mu g\,cm^{-2}$ of pure silver evaporated on to a self-supporting $10\,\mu g\,cm^{-2}$ carbon foil which is mounted a few centimetres in front of the target. The calibration of this sytem was routinely checked against a Faraday cup and found to be reproducible to within $\pm 3\%$. The Ortec Si(Li) X-ray detector is 4 mm in diameter, 4 mm thick, has a $12.7\,\mu m$ thick beryllium window and has an energy resolution of full width at half-maximum = 153 eV at 5.9 keV. A nylon collimator shields the detector from X-rays produced in the beam collimators etc. To minimize both the bremsstrahlung background and the energy of the back-scattered protons, the detector is located at 150° to the beam direction.

To achieve optimum sensitivity for a wide range of elements the H_2Pc targets were bombarded with 1.0 MeV incident protons, which is ideal for the detection of elements having $Z = 11$ to 26, and also with 3.0 MeV protons for analysis of elements with $Z > 20$. In the latter case, a $37.7\,mg\,cm^{-2}$ Kapton absorber was placed in front of the Si(Li) spectrometer to reduce the counting rate due to low energy radiation. The thin-target sensitivity of PIXE at both 1.0 and 3.0 MeV is shown in Fig. 2 [16] and clearly indicates which proton energy should be chosen so as to optimize the sensitivity for any specific range of elements.

The purification procedure is essentially the same as the one described by Wagner *et al.* [13]. The commercial H_2Pc powder was first divided into four 500 mg samples, three of which were placed in clean porcelain crucibles and heated in a furnace to 400° C for one, two and three hours, respectively. Another sample was later prepared under identical conditions for the 4 h heat-treatment. As discussed later, this sample contained more iodine than expected. Aliquots of a few tens of milligrams of each sample were then compacted under 10 tons (10.2 tonnes) pressure without any binding agent, yielding a "target pill" of 1 cm diameter. It is interesting to note that the H_2Pc powder has a bluish colour, but under 10 tons of pressure it acquired a beautiful dark purple colour. It was verified by X-ray diffraction that the high pressure did not induce any modification to the material's structure. The target pills were carefully epoxied on to a 2 cm × 2 cm steel target mount which had a 0.9 cm diameter aperture, and were then magnetically mounted on a vertical multitarget holder capable of holding up to 12 samples. This target holder replaced the carousel shown in Fig. 2.

The 1024-channel X-ray spectra were recorded on a magnetic disc and the areas of the *K* X-ray peaks were then determined using the non-linear least-squares fitting program developed by Campbell *et al.* [18]. The elemental concentrations were subsequently derived from these peak areas using a second program which evaluates the thick target X-ray yields. It takes into account the attenuation of the X-rays in the beryllium window, the gold contact and the dead layer of the Si(Li) detector, the external Kapton absorber (for 3.0 MeV proton bombardments) and also self-absorption in the thick target, to give the X-ray yields for each element considered [18]. For H_2Pc the self-absorption was calculated assuming a matrix containing 75% C, 22% N and 3% H ($C_{32}N_8H_{18}$).

The bombardment time for each target was a compromise between the following factors: adequate counts in the main X-ray peaks, reasonable elapsed time for each target, minimal spectral distorsion due to pile-up, and the maximum beam current that the H_2Pc targets could sustain. Two to three measurements were made at different locations on each target, at both 1 and 3 MeV. Except for two spectra for which the minimum chi-square of the fit to the peaks was poor, the consistency of the results was good, which suggests that the compressed H_2Pc powder targets were uniform.

The d.c. electrical conductivity was measured at 22° C for fields ranging between $\sim 3 \times 10^4$ and $10^6\,V\,m^{-1}$ in a modified Balsbaugh cell (Model ES 32 GR) which applies a slight pressure on aluminium

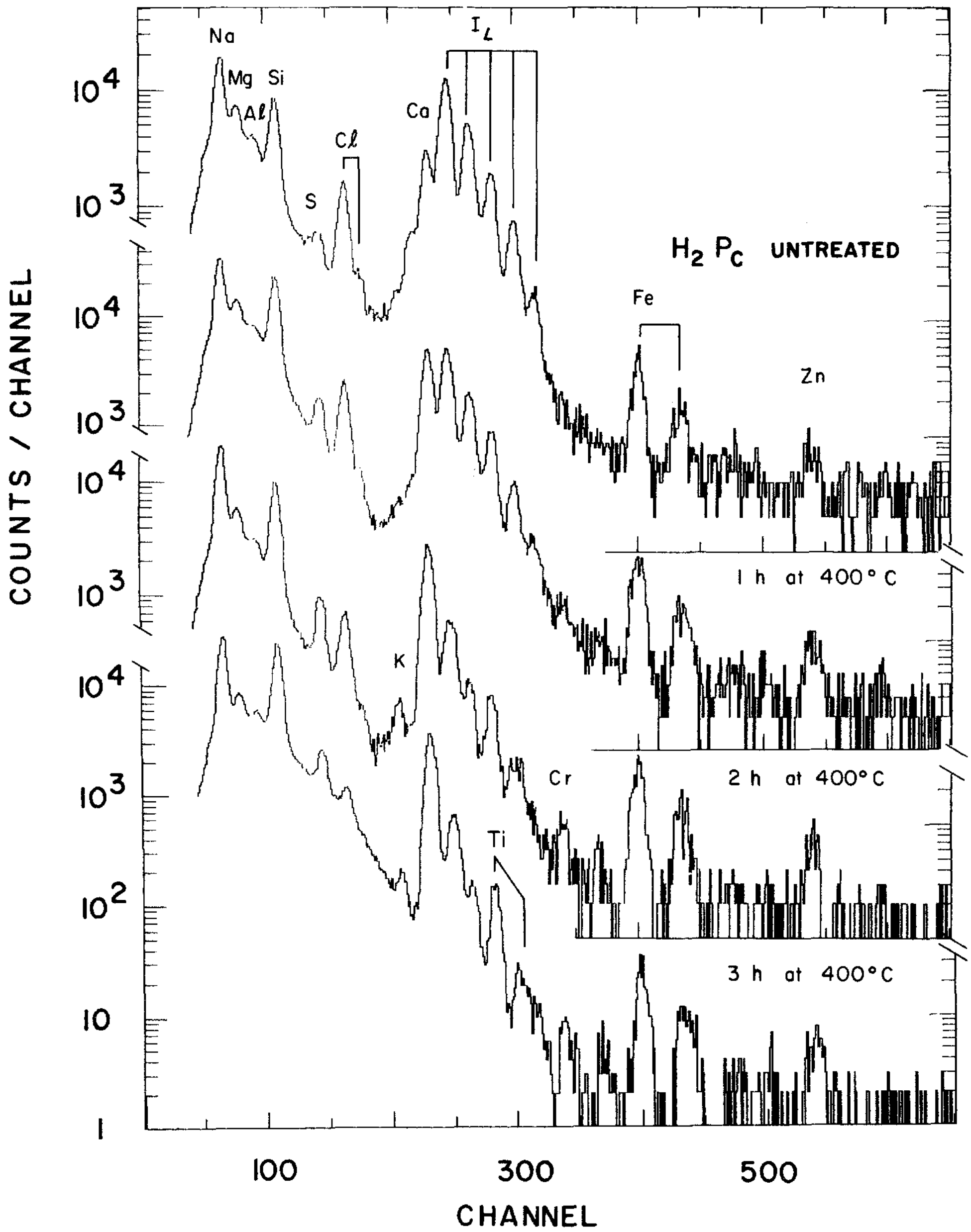

Figure 3 X-ray spectra taken at 1 MeV proton bombarding energy for untreated H_2Pc, and samples heat-treated at 400° C for 1, 2, 3 and 4 h.

electrodes (area of $8 \times 10^{-5}\,m^2$). Dielectric losses ($\tan \delta$) were measured with the same set-up between 70 and 10^4 Hz. Note that the sample heated for 2 h was too small for the electrode system used and its electrical properties were not measured.

3. Impurity measurements by PIXE

The X-ray spectra from untreated and from H_2Pc purified for 1, 2 and 3 h at 400° C and taken at 1 MeV incident proton energy are shown in Fig. 3. The bombardment times were about 25 min per spectrum, during which an average charge of 15 μC was collected. The X-ray peaks are labelled by their chemical element. Because of the strong iodine *L* X-rays in the energy region 3.9 to 4.8 keV, trace quantities of elements such as scandium, titanium and vanadium could not be detected in the untreated H_2Pc; however, traces of titanium can be clearly identified in the 1 MeV spectra from the purified samples (Fig. 3).

Fig. 4 shows the X-ray spectra from untreated commercially available H_2Pc and from H_2Pc purified at 400° C for 3 h, obtained with 3 MeV protons. Note the change of scale in the figure for the iodine *K* X-rays. The spectra shown in Figs 3 and 4 clearly demonstrate the improved sensitivity for low-mass elements at a proton bombarding energy of 1.0 MeV, and for high mass elements at 3.0 MeV, for which the low-energy response was attenuated by a Kapton X-ray absorber.

The elemental concentrations of 19 elements for untreated H_2Pc and for H_2Pc purified at 400° C for 1, 2, 3 and 4 h are presented in Table 1. The uncertainties in the concentrations are 5% for sodium, magnesium, silicon and iodine, 10% for chlorine and iron, and 35% for all other elements except calcium. Due to the overlap of the calcium *K* X-ray peak with the strong iodine *L* X-ray lines, the uncertainty in the calcium concentration is 25%.

The concentrations of impurities such as iodine (1.6%), sodium (0.6%) and calcium (0.13%) found in commercial H_2Pc powder are in agreement with the manufacturer's UV–visible assay of 97% purity [21].

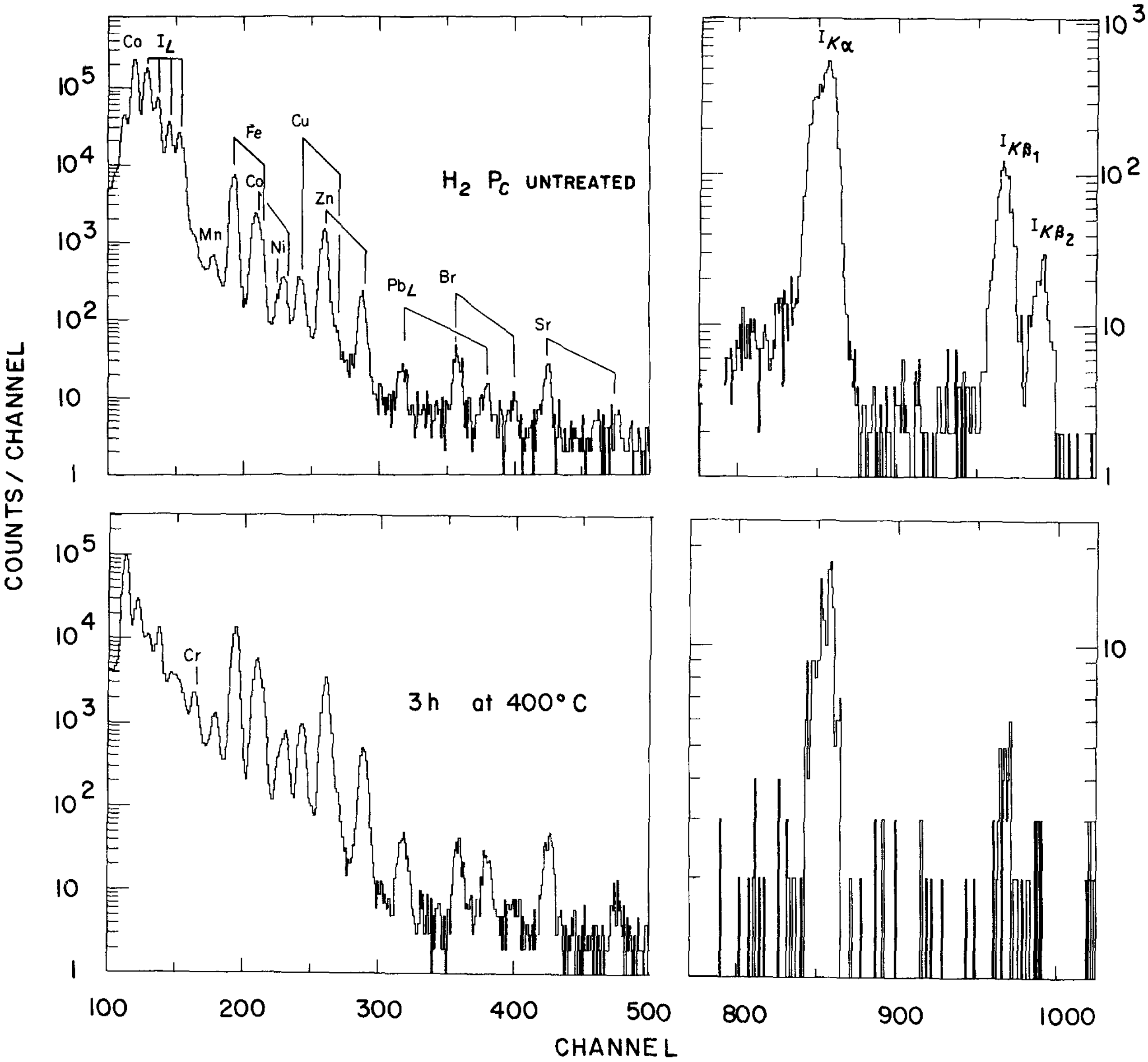

Figure 4 X-ray spectra taken a proton bombarding energy of 3 MeV, for untreated H_2Pc and for a sample which was purified for 3 h at 400° C. Note the change in scale for the iodine K X-ray peaks.

Heating the powder to 400° C for one hour significantly reduced the concentrations of many contaminants. The concentrations of sodium, magnesium, aluminium, chlorine and calcium were reduced by factors between 2 and 5, while the concentrations of elements such as sulphur, potassium, chromium, manganese, iron, cobalt, nickel, copper, zinc, bromine, strontium and lead were not significantly changed by the heat treatment. Except for the highly conducting iodine which was reduced to 520 p.p.m. (i.e. by a factor of 30), extending the heat treatment to two or three hours at 400° C did not significantly affect any of the other impurity concentrations. Surprisingly, the sample heat-treated for 4 h contained more iodine than the one treated for 2 h. We have no explanation for that result. However, note that the total amount of impurities after 4 h of heating is smaller than after 3 h.

It was shown elsewhere [14] that some crystalline impurities (mostly $Ca_5(IO_6)_2$ and HIO_3) could be detected in the H_2Pc by X-ray diffraction. However, after 3 h of heating no impurity peak can be detected, which is not surprising considering their weakness in the original unpurified H_2Pc sample [14].

TABLE I Impurity contents (p.p.m.) in commercially available and in heat-treated metal-free phthlocyanine as determined by PIXE analysis

Element	Untreated		Heated to 400° C			
	Ref. [4]	PIXE	1 h	2 h	3 h	4 h
Na	2960	5966	2224	2975	3500	1626
Mg	< 600	552	165	162	145	128
Al	58	74	19	22	17	29
Si		664	334	291	400	440
S		37	33	46	48	37
Cl	190	276	100	60	65	90
K		3.4	3.5	4	6	2
Ca	1400	1300	800	891	710	650
Cr		(2)	5	6.8	7.5	5
Mn	5.3	5	3	5.2	6.1	5
Fe		75	93	100	82	75
Co		33	38	48	35	25
Ni		2.5	2.6	2.8	2	1
Cu	< 60	7.5	10	13	11	10
Zn		53	55	76	55	38
Br		4	3.3	2.4	4	3
Sr		6	3.3	6.1	6	5
I	17800	15900	3253	580	520	1280
Pb		3	3.9	5.6	4.5	5
Total		24963.4	7158.6	5292.9	4624.1	4454.0

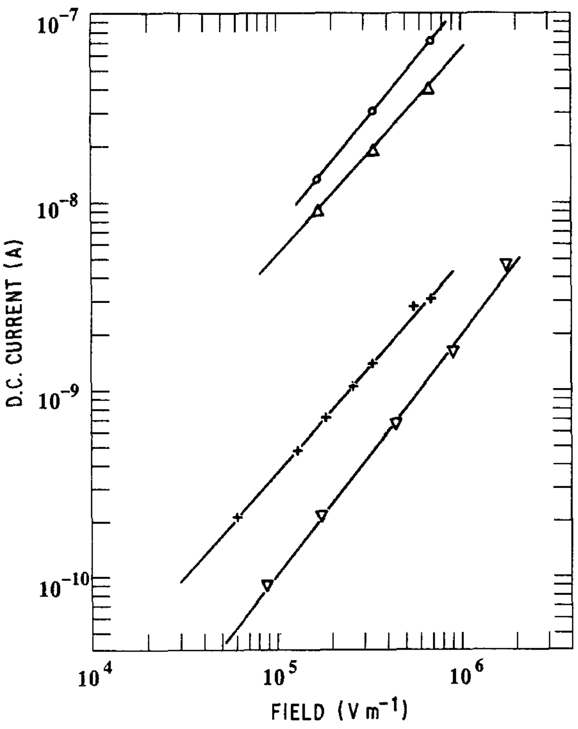

Figure 5 Relation between the current and the electric field for untreated and heat-treated H_2Pc: (○) untreated (slope 1.24), (△) 1 h at 400° C (slope 1.15), (+) 3 h at 400° C (slope 1.13), (▽) 4 h at 400° C (slope 1.38).

4. Electrical measurements

The variations of the d.c. current with the applied fields are shown in Fig. 5 for the various untreated and treated samples. It is obvious that heating at 400° C leads to smaller conduction currents, as expected from the reduced impurity contents shown in Table I. It is also evident that, in the field range used, Ohm's law is not respected and there is no correlation between the slopes in Fig. 5 and the degree of purification. More measurements at higher fields would be required to determine the exact physical process at play, but it may be speculated that the current is affected by space charges.

Dielectric losses as a function of frequency and heating time are shown in Fig. 6. Again the influence of heat treatment is clearly visible, especially for the first 3 h. Note that the influence of heating is significantly lower on losses (a reduction factor of ~ 20 at 100 Hz) than on d.c. conduction (a reduction factor of ~ 100). This suggests that the impurities are not very polar. Interestingly, tan δ slightly increases after 4 h of heating, which corresponds to the larger-than-expected iodine content (see Table I). Thus, it seems that the tan δ value of H_2Pc is especially affected by its iodine content.

On the other hand, the d.c. current continues to decrease after 4 h of heating, even if the iodine content increases. Thus, the conduction process is more sensitive to the total amount of impurity (which decreases with heating time, Table I) than to the iodine content alone. The relation between the current (as measured under 3×10^5 V m^{-1}) and the total impurity content is shown in Fig. 7. Above ~ 8000 to 10 000 p.p.m. of impurities, the current varies slightly with impurities, that is it is a quasi-metallic conduction process. Below that threshold, the current varies exponentially with the impurity content. This is a behaviour typical of a percolation process where charge carriers move between adjacent sites. When the distance between these sites becomes too large (i.e. at low impurity content), carriers cannot jump (or at least very rarely) which results in a current independent of impurity content. This low-conductivity regime has not been observed in our study. Considering the still fairly large amount of impurities present after 4 h of heating (~ 4000 p.p.m.) one may wonder what would be the intrinsic d.c. conductivity of pure H_2Pc.

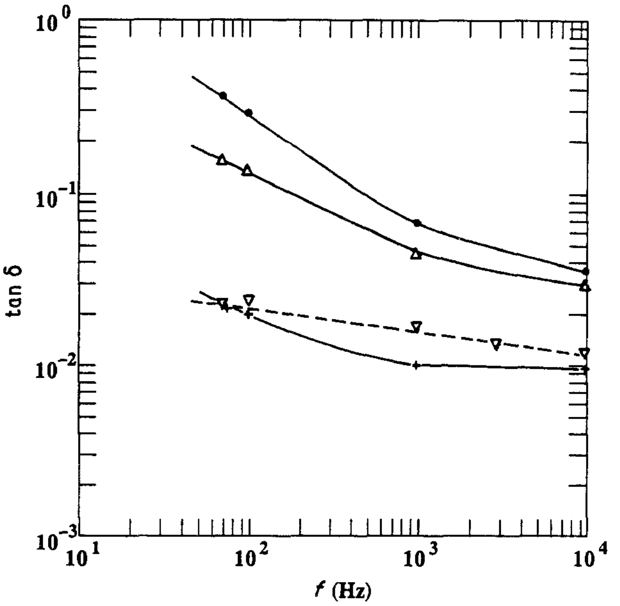

Figure 6 Dependence of tan δ of untreated and heat-treated H_2Pc on frequency and time of treatment: (●) untreated, (△) 1 h at 400° C, (+) 3 h at 400° C, (▽) 4 h at 400° C.

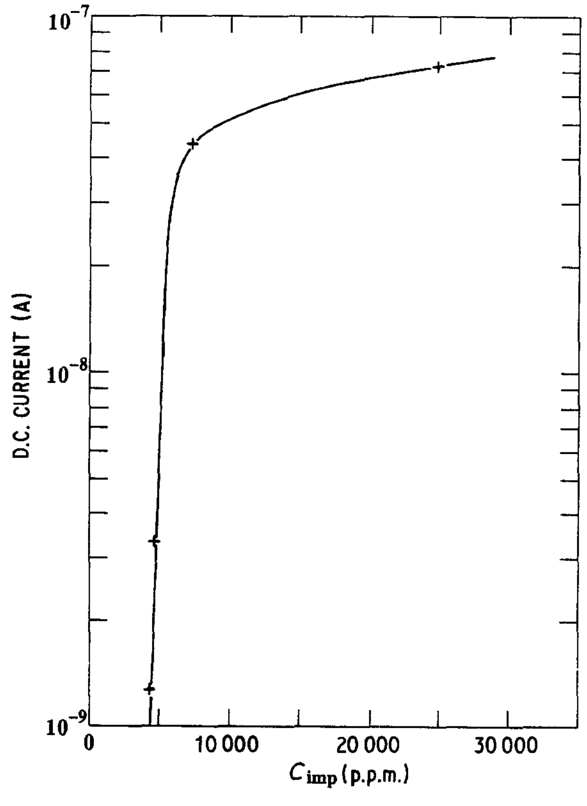

Figure 7 Relation between the current measured at 7×10^5 V m^{-1} (see Fig. 5) and the total amount of impurities (see Table I).

5. Discussion and conclusions

As expected, it was observed in this study that the impurity content (especially iodine) affects the electrical properties of H_2Pc. In fact, the high degree of contamination of commercial H_2Pc explains why its majority carriers are as numerous as in metal-containing phthalocyanines [11]. Note that iodine is often added intentionally in phthalocyanine to increase its conductivity [22] or to modify various properties [15]. Obviously, commercial H_2Pc contains enough iodine without any need for further contamination. The limited influence of impurity content above ~ 10 000 p.p.m. on current suggests that charge carriers in unpurified H_2Pc are mobile in an impurity band rather than in the valence band of the semiconductor.

It is more than likely that the high photoactivity of H_2Pc [23, 24] is largely due to its large iodine content. This is supported by the observation that under vacuum H_2Pc has a different photoemission threshold than after exposure to air; it is quite possible that iodine (or other impurity) reacts with oxygen.

A look at the other major impurities in H_2Pc reveals that they are essentially sodium and calcium, i.e. easily ionizable and reactive impurities. It is, therefore, not surprising that unpurified H_2Pc has a relatively large conductivity and that it increases rapidly with oxidation [15]. In other words, the intrinsic properties of pure uncontaminated H_2Pc have possibly never been measured.

To conclude, it was confirmed by PIXE measurements that large quantities of iodine and other conductive impurities are present in commercial H_2Pc. PIXE has proved to be a rapid and versatile quantitative multi-element analysis tool which is ideally suited for studies of the variation of impurity content with purification procedure. The impurity content in H_2Pc was shown to decrease significantly after a few hours of purification at 400° C, and this resulted in a significant decrease of d.c. conductivity. Dielectric losses also depend, but to a lower extent, on impurities, especially on iodine content. The great influence of impurities on the electrical properties of H_2Pc emphasizes the importance and necessity of measuring the actual impurity content of phthalocyanine samples before reporting any measurement.

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