Fast neutron activation analysis of glycidyl azide polymers

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Abstract. Fast neutron activation analysis technique using 14 MeV neutrons has been applied to analyse nitrogen, chlorine and oxygen content of glycidyl azide polymers (GAP) with Mn around 2100. It has been found that the method is better suited for elemental analysis of GAP than infrared spectroscopy. In fact IR spectral analysis fails to detect chlorine in the polymer when the chlorine content is approximately less than 20%. Oxygen is directly measured by fast neutron activation analysis which is unique.

Keywords. Fast neutron activation analysis; glycidyl azide polymers; polyepichlorohydrin.

1. Introduction

Fast neutron activation analysis (FNAA) uses neutrons of 14 MeV energy to bombard the test specimens to convert different elements in them into radioactive isotopes which decay either by positron (β^+), electron (β^-) or α -emissions and during their nuclear de-excitation process they emit characteristic γ -rays with half life periods around 5–6 min having different energies. The γ -ray spectra are recorded from which the percentage of elements to be estimated can be calculated using a monitor of known elemental composition. The method is fast, fairly accurate and capable of estimating several elements simultaneously.

FNAA has not been widely used to analyse polymers. Bhoraskar (1980) used it to analyse fluorine in polytetrafluoroethylene. Panda and Kulkarni (1988) employed the method for the analysis of nitrogen in cellulose nitrate, amine cured epoxy resins, Schiff-based oligomers and nylon-6. They also estimated chlorine content of PVC by FNAA. However the method has been used to analyse various other materials including aluminium in aluminized explosives and rocket propellants and nitrogen in various explosives (Kulkarni and Bhoraskar 1988; Kulkarni *et al* 1988, 1989a, b; Panda and Kulkarni 1991).

Glycidyl azide polymers which are used as energetic plasticizers in double base rocket propellants, fuel binder in composite propellants (Sutton 1992) and as fuel rich propellants in integrated ram rocket engines (Kubota *et al* 1991) are interesting low molecular weight polymers which have nitrogen, chlorine and oxygen to be simultaneously determined by FNAA. Such analysis by other chemical methods are laborious, time consuming and not very accurate.

1.1 Theory

Principles of fast neutron activation analysis and nuclear reaction fast neutrons are generated by bombarding a tritium target with accelerated deuterium ions according to

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the following nuclear reaction

The reaction cross-section (σ) for the above reaction is 5 barns. These 14 MeV neutrons are focussed on the sample materials to convert the elements in them into their radioactive isotopes which subsequently decay by γ -emission.

1.1a *Determination of the amount of a given element in a particular sample (Arnikar 1990):* Let x g of sample containing N atoms of the element be placed in a uniform flux of thermal neutrons for time t to produce measurable activity, say A_t . It is presumed that the activity A_t is solely due to isotope under study. The activity produced is given by:

$$A_t = N\Phi\sigma(1 - e^{-\lambda t}), \quad (1)$$

where N is the no of atoms of the target element, Φ the neutron flux, σ the neutron capture cross section, λ the decay constant (sec^{-1}) and t the time of irradiation.

A_t = activity produced if measured immediately at the end of irradiation. At time = t' , activity will be

$$A'_t = A_t \cdot e^{-\lambda t'}$$

or

$$A'_t = N\Phi\sigma(1 - e^{-\lambda t})e^{-\lambda t'}. \quad (2)$$

From (2) the weight w g of the particular element present in the x g of the sample is known from

$$W = MN/L = (M/L)(A'_t/\Phi\sigma(1 - e^{-\lambda t})e^{-\lambda t'}), \quad (3)$$

where M is the atomic wt of the test element and L the 6.022×10^{23} . In analysis of an unknown sample, a monitor material with known elemental composition is used. If in the monitor, w' g of an element to be determined in the unknown sample is present then,

$$w/w' = A_t^*/A_{t'}^*, \quad (4)$$

where w is the weight of the element present in the test sample to be determined, w' the weight of the same element in the monitor, A_t^* the γ -activity induced due to the test element and $A_{t'}^*$ the γ -activity induced due to the same element in the monitor.

However the monitor can have an element other than the element to be determined in the test sample provided the radioactive isotope formed by the monitor element on neutron irradiation has comparable half life period ($\bar{t}_{1/2}$) for decay with that of the test sample but different energy for γ -emission. Such elements can sometimes monitor neutron analysis of more than one element in the test samples. Therefore if x_1 g of an unknown sample is taken with x_2 g of monitor where w_1 and w_2 are the weights of the elements to be determined in the test sample and monitor respectively, we get

$$w_1/w_2 = K(A_{t_1}/A_{t_2}),$$

where A_{t_1} activity induced due to test element, A_{t_2} the activity induced due to monitor

element and K the activation constant.

$$K = \frac{M_1}{M_2} \left\{ \frac{x_1 \sigma_1 (1 - e^{-\lambda_1 t}) e^{-\lambda_1 t'}}{x_2 \sigma_2 (1 - e^{-\lambda_2 t}) e^{-\lambda_2 t'}} \right\}.$$

The terms in the above expression have their usual significance already defined earlier.

2. Experimental

2.1 Materials

Glycidyl azide polymers (GAP) were synthesized by reacting polyepichlorohydrin (PECH) with sodium azide in dimethyl sulphoxide for 11 h at 100°C (Tokui *et al* 1990). The details of the synthesis and purification have been discussed (Panda *et al* 1996). PECH in turn was synthesized using BF_3 -etherate as the catalyst with methylene chloride as solvent at 20°C for different specified periods after Biedron *et al* (1991). PECH diols were better synthesized by using BF_3 -ethylene glycol complex as the initiator (Biedron *et al* 1991). The number average molecular weight, $\bar{M}_n$ of GAP was around 2100.

2.1a Fast neutron activation analysis method: The FNAA facilities available at the Department of Physics, University of Poona were utilized. The details of the fast neutron generator have been described (Bhoraskar 1989).

2.2 Estimation of nitrogen

The estimation of nitrogen was carried out by irradiating for 5 min a mixture of known quantities of the test sample and aluminium powder (aluminium in the mixture acts as a monitor) packed in a polyethylene vial with 14 MeV neutrons having neutrons flux of 10^8 neutrons/cm² sec. Nitrogen undergoes the following nuclear reaction:

The reaction cross-section σ , for the above reaction is 5.7 millibarns. The half life period ($t_{1/2}$) of ^{13}N is 9.96 min and the γ -energy, E_γ is 0.511 MeV. Aluminium undergoes the following nuclear reactions with fast neutrons.

A pneumatic system was used to transfer the sample from irradiation head to γ -ray detector. The induced γ -ray activity was measured with a HPG detector coupled to a 4096 multi channel analyser. The concentration of the test element in the sample was estimated by measuring the activity under the photo peak using a computer software. The nitrogen content was determined by using the following formula

$$W_N/W_{Al} = K(A_N/A_{Al}).$$

where W_N is the weight of nitrogen in the test sample (to be determined), W_{Al} the weight of aluminium as monitor, A_N the activity or counts induced due to nitrogen under the photopeak of 0.511 MeV and A_{Al} the activity or counts induced due to aluminium under the photopeak of 0.84 MeV.

K is the activation constant which was determined using an authentic sample of sodium nitrate with known nitrogen content following the similar procedure discussed above.

2.3 Estimation of chlorine

Chlorine in the test sample was determined by using manganese (in the form of MnO_2) as the monitor element adopting the same procedure as discussed for the estimation of nitrogen. The irradiation time, however was kept five min instead of ten min. The relevant nuclear reactions of chlorine and manganese with 14 MeV neutrons are represented below:

$$^{37}Cl(n, p)^{37}S, \sigma, 40 \pm 3 \text{ mb}; \quad t_{1/2}, 5.08 \text{ min}; \quad E_\gamma, 3.09 \text{ MeV.}$$

$$^{55}Mn(n, \alpha)^{52}V, \sigma, 52 \text{ mb}; \quad t_{1/2}, 3.76 \text{ min}; \quad E_\gamma, 1.434 \text{ MeV.}$$

The chlorine content was determined using the following formula,

$$W_{Cl}/W_{Mn} = K(A_{Cl}/A_{Mn}),$$

where W_{Cl} is the weight of chlorine in the test sample, W_{Mn} the weight of manganese in the monitor, A_{Cl} the activity or counts induced due to chlorine under the photopeak of 3.09 MeV and A_{Mn} the activity or counts induced due to manganese under the photopeak of 1.434 MeV.

The activation constant was predetermined by using sodium chloride as the authentic sample for chlorine by adopting the similar procedure as discussed earlier.

2.4 Estimation of oxygen

The oxygen content in the test sample was determined using sodium as the monitor (in the form of NaCl) and following exactly the similar procedure given for nitrogen except for the irradiation time which was kept at 30 sec in this case instead of 10 min. The nuclear reactions of oxygen and sodium with 14 MeV neutrons are given below:

$$^{16}O(n, p)^{16}N, \sigma, 42 \pm 3 \text{ mb}; \quad t_{1/2}, 7.35 \text{ sec}; \quad E_\gamma, 6.13 \text{ MeV}$$

$$^{23}Na(n, \alpha)^{20}F, \sigma, 150 \pm 14 \text{ mb}; \quad t_{1/2}, 11.5 \text{ sec}; \quad E_\gamma, 1.63 \text{ MeV.}$$

The oxygen content was determined by using the following formula,

$$W_O/W_{Na} = K(A_O/A_{Na}),$$

where W_O is the weight of oxygen in the test sample, W_{Na} the weight of sodium in NaCl, A_O the activity or counts induced due to oxygen under the photopeak of 6.13 MeV, A_{Na} the activity or counts induced due to sodium under the photopeak of 1.63 MeV and K the activation constant predetermined using sodium as the monitor.

2.5 IR spectral analysis

IR spectral analysis of PECH and GAP were carried out by recording the spectra of smears of polymers on a NaCl window with the help of a Perkin-Elmer No 221 double beam spectrometer.

3. Results and discussions

The elemental compositions of PECH from which they are made and the extent of conversion of the $-\text{CH}_2\text{Cl}$ group of PECH to $-\text{CH}_2\text{N}_3$ group of GAP is shown below:

The formation of GAP from PECH was followed by recording the IR spectra of different aliquotes during the above synthesis which prolonged for 11 h. It is interesting to note that after around 7 h of the reaction, the IR absorption peak at 745 cm^{-1} due to $-\text{CH}_2\text{Cl}$ group in PECH becomes completely flat as shown in figure 1. This is accompanied by the appearance of a very strong absorption at 2100 cm^{-1} due to $-\text{CH}_2\text{N}_3$ group. It is misleading to believe that all $-\text{CH}_2\text{Cl}$ have reacted out to form $-\text{CH}_2\text{N}_3$ where IR absorption at 745 cm^{-1} is absent in GAP. In the patent literature (Tokui *et al* 1990), 11 h of reaction to convert PECH to GAP in DMSO has been recommended where chlorine content in GAP is reported to be 2%. This necessitated to find out the chlorine content in different samples of GAP prepared with different duration of conversions beyond 7 h of reaction of PECH with sodium azide in DMSO at 100°C using FNAA. It is very interesting to note that a substantial amount of $-\text{CH}_2\text{Cl}$ remains in GAP after 7 h of conversion which demanded prolonging the reaction period. Table 1 gives the nitrogen, chlorine and oxygen content of different PECH and GAP samples measured by FNAA. From a large number of measurements carried out for compounds containing nitrogen, oxygen and chlorine not reported in this paper, we have come to the conclusion that the method is accurate within 2–3% of error. However for polymer samples the error goes upto 5% mostly due to the difficulty in determination of the exact molecular weight of the polymers needed for obtaining values for elemental compositions. Similar accuracy is reflected in the values of chlorine and oxygen content in PECH 1 and PECH 2 reported in table 1. Their conversion to azide polymers whose nitrogen content steadily increasing to a maximum value was compared with results available in patent literature (Tokui *et al* 1990). Our results for the final nitrogen content of GAP were lower from the values in the literature by a margin of about 2%.

After 11 h of conversion the decrease in chlorine content with reaction period becomes asymptotic with the time axis. However in our analysis, the chlorine content of 3.3% was left out of GAP with a nitrogen content of 40.15% after 11 h of reaction (figure 2).

The oxygen content of PECH depends upon the catalyst used to polymerize epichlorohydrin. BF_3 -etherate is unlikely to give a GAP diol with $-\text{OH}$ groups at the two ends of the polymer chain. It can be better obtained by using BF_3 -ethylene glycol complex (Biedron *et al* 1991).

Figure 1. IR spectra of the reaction products of PECH with sodium azide at different time intervals (t): a. $t = 0$, b. $t = 5$ h and c. $t = 7$ h.

Table 1. Elemental analysis of nitrogen, chlorine and oxygen in GAP by FNAA.

Sample	No. of h of reaction with sodium azide	Nitrogen (%)	Chlorine (%)	Oxygen (%)
PECH 1	—	0.00	40	21
GAP 1A	7	13	28	18
GAP 1B	8	25	16	20
GAP 1C	9	28	13	18
PECH 2	—	0.00	42	17
GAP 2A	10	39	5.0	16
GAP 2B	11	40.15	3.3	16

The PECH and corresponding GAP whose analysis is reported in table 1 were all made using BF_3 -etherate as the catalyst. Thus we apprehend the variation of $-\text{OH}$ end groups in all the samples particularly those of PECH. The theoretical oxygen content of a GAP diol of $\bar{M}_n$ 2100 should be 16.7 if the $-\text{OH}$ functionality is 2.

Figure 2. γ -ray spectrum of GAP (2B).

It is rather difficult to predict $-\text{OH}$ functionality of the polymers from their oxygen content as reported in table 1 with any substantial accuracy. Nevertheless, the method is indicative of the oxygen content of the polymers to a rough measure.

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