Gas Chromatographic Determination of Carbide Carbon in Aluminium Nitride

A P WALVEKAR & M SANKAR DAS*
Analytical Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085

Received 6 January 1986; revised and accepted 7 April 1986

A gas chromatographic method for the determination of carbide carbon in aluminium nitride is described. The sample is decomposed with 40% sodium hydroxide and the methane thus evolved is oxidised to carbon dioxide, which is then determined gas chromatographically using a thermal conductivity detector. For an average value of 26.6 µg of carbide carbon (8 determinations) the standard deviation is 0.8 µg. The limit of detection is 1.3 µg and the limit of quantitation is 4 µg of carbide carbon for 1 g of a sample.

Carbon-14 is an important radionuclide for the preparation of labelled organic compounds useful in chemical and biochemical investigations. It is prepared by neutron bombardment of $^{14}\text{N}$ (Eq. 1).

$$^{14}\text{N} + ^{1}\text{H} \rightarrow ^{14}\text{C} + ^{1}\text{H} \quad \ldots (1)$$

For this purpose the nitride of aluminium is preferred over beryllium nitride for irradiation in a nuclear reactor because of the high cost and toxicity of beryllium nitride. Carbon-14 of high specific activity is necessary for most of its applications which require that the target must have a low C-12 content. Hence the estimation of carbide carbon content in aluminium nitride is essential.

The reported methods for the determination of carbide carbon in metallic beryllium, aluminium and aluminium nitride involve decomposition of the sample with acid or alkali and the determination of the methane evolved due to hydrolysis of the carbide carbon. The evolved methane is oxidised to carbon dioxide by passing over heated copper oxide and measured by gravimetry, gasometry, conductometry or non-aqueous titrimetry. The evolved methane has also been determined directly by gas chromatography using a flame ionization detector (FID). The present paper describes the standardisation of a gas chromatographic method for the determination of carbide carbon in aluminium nitride released as methane on alkali decomposition.

Materials and Methods

Apparatus

The apparatus essentially consisted of (i) the nitrogen purification section, (ii) the sample processing section and (iii) the measurement section. A schematic diagram of the apparatus is given in Fig. 1 and that of sample injection system in Fig. 2. Commercial nitrogen (A) was freed from impurities such as hydrocarbons, moisture and carbon dioxide by passing over copper oxide (C) at 900°C and then over molecular sieve 5 A (D). The sample was decomposed in the reaction flask (H) fitted with a reflux condenser (I) and a dropping funnel (G). It had an inlet stop-cock (F) for nitrogen and an outlet stop-cock (J) for the mixture of evolved gases and nitrogen. The mixture of gases coming out from the reaction flask was passed through a series of traps consisting of (i) a tube packed with copper sulphate loaded silica gel (K) for removal...
of ammonia, (ii) a tube packed with anhydrous magnesium perchlorate and ascarite (L) for removal of moisture and carbon dioxide, (iii) a combustion tube packed with copper oxide (M) at 900°C where methane was oxidised to carbon dioxide, (iv) a tube packed with anhydrous magnesium perchlorate (N) for removal of moisture generated in the oxidation reaction and finally a U-shaped sample tube (O) cooled in liquid nitrogen bath where carbon dioxide was frozen. The guard tube packed with molecular sieve 5A (P) prevented any atmospheric moisture or carbon dioxide from entering the sample tube. The carbon dioxide, preconcentrated in the sample tube (O) as described above, was injected into a gas chromatograph for its determination.

A home made gas chromatograph equipped with a thermal conductivity detector (TCD) having a matched pair of thermistors in the bridge circuit and a copper column (1 m × 3.2 mm int. diam.) packed with Porapak Q (80-100 mesh) was used. Hydrogen (flow rate 30 ml min⁻¹) was used as a carrier gas and the bridge current was maintained at 10 mA.

Reagents

All reagents were of AR grade and the solutions were prepared in distilled water. Copper sulphate loaded silica gel was prepared by equilibrating silica gel (60-120 mesh) with a saturated solution of copper sulphate in distilled water. The supernatant solution was decanted and the copper sulphate loaded silica gel dried at 110°C.

Procedure

An appropriate amount (0.2-1.0 g) of finely powdered aluminium nitride was placed in the reaction flask. Sodium hydroxide solution (40%, 50 ml) was taken in the dropping funnel. Nitrogen was allowed to flow at the rate of 60 ml min⁻¹ and the apparatus was thoroughly flushed with nitrogen. Stopcocks (J) and (F) were closed. The reaction flask was evacuated and for this purpose stopcock (J) was connected to the vacuum line and then closed after evacuation. Sodium hydroxide solution (50 ml) was introduced into the reaction flask and stopcocks (F) and (J) were rotated to restore the flow of nitrogen. The reaction was accelerated by heating the mixture to boiling. When the reaction was complete and carbon dioxide was completely frozen in the sample tube (30 min were found to be sufficient), the sample tube part was disconnected from the system at the inlet of magnesium perchlorate trap (N). After the nitrogen present in the sample tube was flushed out with hydrogen, the tube was closed at both the ends and removed from the liquid nitrogen bath and connected to the gas chromatograph for the measurement of the carbon dioxide.

Blank Determination

A blank determination was carried out exactly as described above but without the sample.

Calibration

Appropriate amounts of methane in the range of 10-100 μl were injected into the system through the injection port (E) by means of a gas-tight syringe and gas chromatographic measurements for carbon dioxide were carried out. A calibration graph of peak height versus volume of methane was plotted and used for the analysis.

Results and Discussion

Experiments to study the decomposition of aluminium nitride were performed using different reagents such as (i) 85% phosphoric acid, (ii) 1:1 phosphoric acid, (iii) phosphoric acid + sulphuric acid (1:1) and (iv) 40% sodium hydroxide or potassium hydroxide solution. An appropriate amount of the sample was heated to boiling in each case. Almost identical results were obtained for the carbide carbon content in a given sample when it was decomposed with any of the above mentioned reagents. Since the decomposition with alkali was faster compared to the acidic reagents it was preferred. The reaction can be represented by Eq. (2).

Al₄C₃ + 4 NaOH + 4 H₂O → 3 CH₄ + 4 NaAlO₂ … (2)

Athavale et al.⁵ used 60% sulphuric acid for the decomposition of aluminium nitride and adopted conductometry for the determination of carbon dioxide. They reported an average blank value of 26 μg of carbide carbon for a number of blank determinations. In the reported methods for the determination of carbide carbon in metals⁷⁻⁹ flame ionization detector (FID) was used for the measurement of methane evolved when the sample was decomposed with acid or alkali in an evacuated reaction flask. FID being sensitive for the measurement of methane a small aliquot of the total evolved gas was used for the analysis. In the present work the evolved methane was oxidised to carbon dioxide by passing over copper oxide at 900°C and determined subsequently by gas chromatography using a thermal conductivity detector (TCD). TCD was preferred for the analysis as it is simple and rugged in its operation compared to FID. The entire evolved methane was separated from other gases by passing through various traps as previously described and converted into carbon dioxide thus compensating reasonably for the lower sensitivity of TCD. The ammonia evolved in the reaction was trapped using copper sulphate loaded silica gel. This dry trap for
ammonia is preferable as, unlike an acid solution, it does not release moisture into the stream of nitrogen. The progress of the reaction is indicated by the silica gel which changes its colour to deep blue as ammonia evolved in the reaction passes over it.

Two samples of aluminium nitride procured from the Chemistry Division, BARC were analysed in replicate in order to determine the precision of the method and the results are given in Table 1.

The experimental data were treated statistically for estimating the limit of detection for a determination using student ‘t’ value (99.5% CL.) appropriate for 10 determinations and the limit of quantitation defined by the American Chemical Society12. It has been reported11 that if the carbide impurity in aluminium nitride is below 30 ppm, it is possible to get adequate specific activity of carbon-14. The limit of quantitation of 16 ppm, using 0.25 g sample, obtained in the present work is well below this limit.

Acknowledgement
The authors are thankful to Dr T P Radhakrishnan and Shri TS Krishnamoorthy for their helpful suggestions during the preparation of the manuscript.

References