

SYNTHESIS, PURIFICATION, STORAGE AND ISOTOPIC ANALYSIS  
OF  $CT_4$  ON THE MULTICURIE SCALE

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## SUMMARY

Multicurie amounts of  $CT_4$  were prepared from  $T_2$  via a two-steps synthesis with an overall yield of ca. 75%. After purification, the radio gas chromatographic analysis of the product revealed only a 0.5%  $T_2$  (or HT) impurity. The isotopic analysis, carried out independently by mass spectrometry and by high-resolution gas chromatography, showed that, immediately after preparation, tritiated methane contained over 97.8 mol%  $CT_4$ , with only traces of partially tritiated methanes. However self radiolysis, in particular fast intermolecular H/T scrambling, caused severe storage problems. Even after dilution with a thousand-fold excess of  $CH_4$ , radiation-induced isotopic exchanges led to serious contamination of  $CT_4$  by partially tritiated methanes. A dramatic improvement was obtained, without further dilution of  $CT_4$ , by addition of 1 - 2 mol%  $NH_3$ , which completely suppressed radiolytic H/T scrambling. A preparative gas chromatographic technique was developed, which allows isolation of  $CT_4$  in a state of high radiochemical and isotopic purity.

Introduction

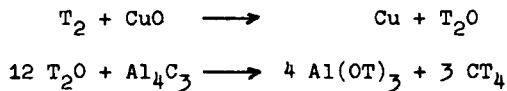
The interest for  $CT_4$  dates back to the introduction of the decay technique for the mass spectrometric and kinetic study of organic ions in a variety of gaseous and condensed systems (1), since  $CT_4$  represents the precursor of the extensively investigated  $CT_3^+$  cation.

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The only method so far described for the preparation of  $CT_4$  is based on the oxidation of  $T_2$  with  $CuO$ , followed by the reaction of the tritiated water formed with  $Al_4C_3$  (2). The method, specifically designed for the preparation of limited activities of high-purity  $CT_4$ , where the yield does not represent a factor of prime concern, proved consistently successful in its applications by different laboratories during the past decade (3-8).

However, the growing number and variety of the investigations concerning the decay ions (9), in particular their foreseeable preparative applications, require the synthesis of considerably larger amounts of  $CT_4$ , and the development of purification, storage, and analytical procedures adequate to the much higher activities involved. As the reaction sequence:



was still regarded as the most convenient among the available routes to  $CT_4$  (10-19), an attempt was undertaken to scale up the original procedure of Ciranni and Guarino (2) to the preparation of multi-curie amounts of isotopically pure  $CT_4$ , essentially by improving the overall yield by at least an order of magnitude.

### Experimental

Materials. Tritium gas with a stated purity of 99 mol% was obtained from CEN (Mol, Belgium). As an excessive contamination by decay-formed  $^3He$  was found detrimental, only samples of recent preparation (ca. 2 months) were used. Copper oxide was a pro-analysi product from Merck, while aluminum carbide from Fluka AG had a minimum purity of 92 mol%.

Apparatus and procedure. The pyrex apparatus shown in Figure 1 was designed according to the concept of replacing the slow

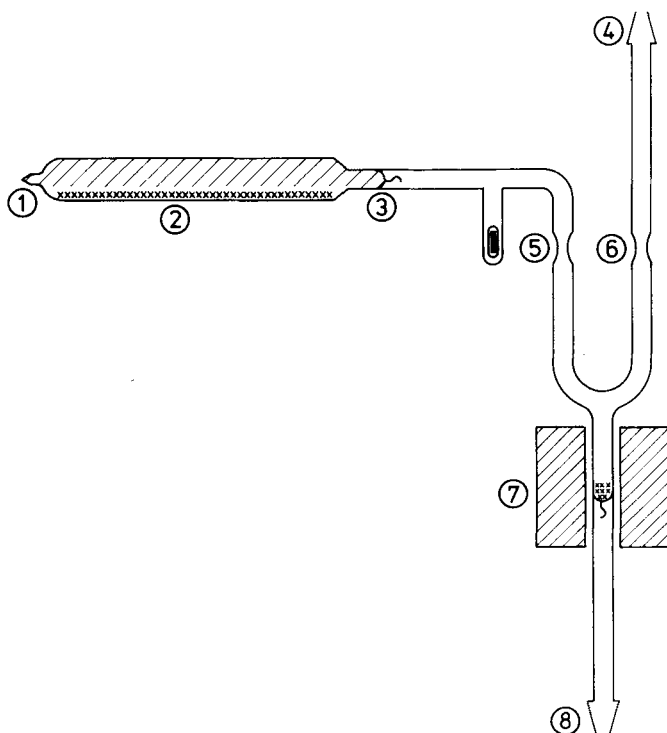


Figure 1: Apparatus for the preparation of  $CT_4$ .

spontaneous diffusion of the gaseous reagents typical of previous preparation (2) by their forced transfer onto the appropriate solid reagents, in order to increase the conversion achievable in the relatively short time allowed to the reaction by the fast self-radiolysis of the product.

A weighed amount of  $CuO$ , in the ratio of ca. 100 mg per 10 Ci of  $T_2$ , was introduced into vessel 2 through the initially open arm 1, that was then connected to a vacuum line. The vessel was thoroughly outgassed by heating for 3 hours, at  $300^\circ C$  under  $10^{-3}$  torr. After cooling, the desired amount of  $T_2$  was introduced into vessel 2 through arm 1, which was then sealed off. Oxidation of tritium to  $T_2O$  was achieved by heating vessel 2 for 16 hours at  $450^\circ \pm 10^\circ C$ . The apparatus was then connected to a vacuum line via joint 4 and

thoroughly outgassed. A weighed amount, ca. 150 mg per 10 Ci of  $T_2$ , of finely pulverized  $Al_4C_3$  was introduced from joint 4, care being taken to avoid contamination of the pyrex walls near constriction 6. Aluminum carbide was then outgassed at  $10^{-3}$  torr by heating it at  $350^\circ C$  for 3 hours with the tubular oven 7. After cooling, the stopcock connecting joint 4 to the vacuum line was closed, the U-shaped section was immersed into liquid nitrogen, and the break-seal 3 broken with the pyrex-enclosed magnetic hammer, thus allowing the  $T_2O$  contained in vessel 2 to condensate over  $Al_4C_3$ . The quantitative transfer of  $T_2O$  into the liquid-nitrogen cooled section was accomplished by gradually opening the stopcock connecting joint 4 to the vacuum line, until the pressure within the apparatus dropped below  $10^{-3}$  torr. Constrictions 5 and 6 were then sealed off, the U-shaped section containing the  $Al_4C_3$ - $T_2O$  reagents was allowed to warm up, before being heated to  $160^\circ \pm 5^\circ C$  in a thermostatically controlled oven for 2 hours. Joint 8 was then connected to a Töpler pump. The apparatus, now mounted with the 5 and 6 seals pointing downward, was cooled to  $-78^\circ C$  to trap any unreacted  $T_2O$ , its last break-seal was opened, and the crude reaction product was pumped into a volumetric bulb, to measure its yield. Immediately, afterwards, the active gas was diluted with an excess of high-purity ( $> 99.9995$  mol%)  $CH_4$ , obtained from Edelgas GmbH. Some of the  $CH_4$  was introduced into the reaction apparatus, in order to wash out and recover any  $CT_4$  adsorbed on the walls, or on the  $Al_4C_3$ .

Purification of the crude product. According to Ciranni and Guarino (2), tritiated methane can be purified by adsorption on activated  $5 \text{ \AA}$  molecular sieves at  $-160^\circ C$ , under conditions where the major impurities,  $HF$  and  $T_2$ , are not appreciably retained and can be easily washed out with inactive hydrogen. It was found that, while extremely effective, this procedure caused appreciable losses

of  $CT_4$ , since some of the methane can hardly be desorbed from molecular sieves even at higher temperatures. The use of activated silica gel at liquid nitrogen temperature, recommended by Pritchard, Pyke and Trotman-Dickenson (20), appeared to provide effective purification of methane from HT,  $T_2$  and tritiated water, while allowing nearly quantitative recovery of the labelled methane.

Radiochemical analysis. The purity of the product was assayed by radio gas chromatography, using a Model 7620A Hewlett-Packard Research gas chromatograph, equipped with a 2-m long, 4-mm i.d. 5 Å molecular sieves column, operated at 55 °C, with nitrogen as the carrier gas at a flow rate of 86 ml/min. The effluent from the column, diluted with  $CH_4$ , was fed into a 10-ml internal-flow proportional counter from Berthold Frieseke, connected both to a ratemeter with a strip chart recorder for analogous display, and to a Berthold Frieseke LB 2520 counter-timer with a Teletype printer for digital recording.

Isotopic analysis. Two independent methods were used to determine the isotopic composition of tritiated methane. In general, the samples submitted to analysis were gaseous solutions of the crude tritiated product diluted with a thousand-fold excess of high-purity  $CH_4$ .

Mass spectrometry. A complete analysis of the mass region of interest ( $m/e$  values from 15 to 25) was carried out for each sample with an AEI MS702 mass spectrometer. In order to eliminate the problems associated with isotopic discrimination in molecular fragmentation, attention was focused on parent ions, and the energy of the ionizing electron beam was accordingly kept at a low (20 eV) value. In particular, the ionic intensities at  $m/e$  24, 22, and 20, correspondent respectively to the parent ions of  $CT_4$ ,  $CHT_3$  and  $CH_2T_2$ , were recorded and referred to the intensity of the base peak,  $CH_4^+$ .

In all cases, suitable background corrections were obtained from blank analyses, carried out under identical conditions on samples of  $\text{CH}_4$  not containing tritiated methane. The most accurate results were obtained in the measurement of the  $\text{CT}_4^+/\text{CH}_4^+$  intensity ratio, since the  $\text{CT}_4^+$  determination referred to a relatively abundant component, was performed in a mass region remarkably free from interfering ions, as shown by the low and reproducible background, and was not complicated by the fragment ions from heavier methane molecules. In fact, the  $\text{CT}_4/\text{CH}_4$  ratio deduced from the mass spectrometric analysis was found in excellent agreement with the values obtained from gas chromatography and from activity measurements.

The determination of  $\text{CHT}_3$  and  $\text{CH}_2\text{T}_2$  is complicated by the occurrence of mass doublets at  $m/e = 22$  ( $\text{CHT}_3^+ - \text{T}_2\text{O}^+$ ) and at  $m/e = 20$  ( $\text{CH}_2\text{T}_2^+ - \text{HTO}^+$ ). Nevertheless, the high resolution and sensitivity of the instrument provided results in good agreement with those from gas chromatography, despite the low abundances of  $\text{CHT}_3$  and  $\text{CH}_2\text{T}_2$  with respect to  $\text{CT}_4$ . On the other hand, the determination of  $\text{CH}_3\text{T}$  proved impossible, as the minor  $\text{CH}_3\text{T}^+$  ion was obscured by a large background peak due to water.

Gas chromatography. The gas chromatographic resolution of all tritiated methanes was carried out as described by Bruner, Cartoni and Possanzini (21), using a 64-m long, 0.22-mm i.d. soft glass capillary column, whose inner walls had been chemically etched with NaOH to obtain a layer of active silica. Before use, a stream of  $\text{N}_2$ , saturated at  $0^\circ\text{C}$  with water vapour, was passed through the column for 72 hours, in order to achieve a controlled deactivation of the  $\text{SiO}_2$  layer. The separation was performed at  $77^\circ\text{K}$ , using a mixture of He and  $\text{N}_2$ , in the 3:7 molar ratio, as the carrier gas, at flow rates from 0.20 to 0.70 ml/min, the outlet of the column being connected to the flow counter previously described.

A typical performance of the column is illustrated in Figure 2, showing the full resolution of  $CH_3T$  and  $CH_2T_2$ , and the entirely adequate separation of the  $CHT_3/CT_4$  pair. The only drawback of the analysis arised from the long time required, which could reach 40 hours for  $CT_4$  elution.

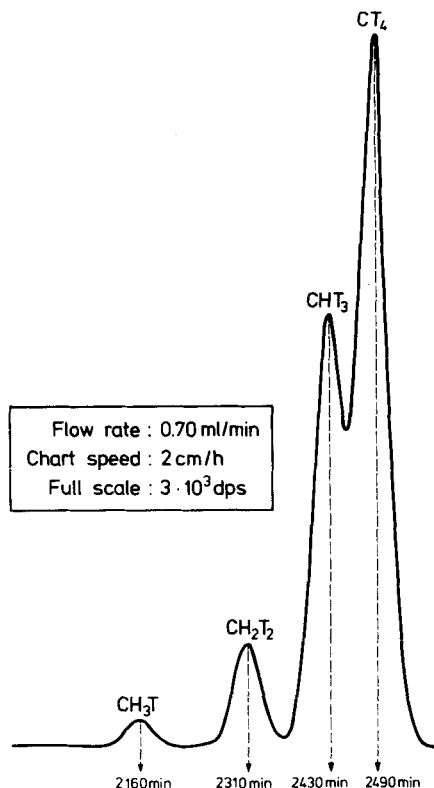


Figure 2: Radio gas chromatographic analysis of isotopic tritiated methanes.

### Results

Yields and purity of  $CT_4$ . The yields of tritiated methane, based on  $T_2$ , were measured with several independent methods. For preparations involving at least 10 Ci of  $T_2$ , volumetric measurements of the gaseous product gave an average yield of  $65 \pm 15\%$ , the scatter of the data arising mainly from the large errors in pressure

readings. Somewhat more precise data were obtained measuring the activity of known aliquots of the product with a calibrated proportional counter, leading to an average yield of  $70 \pm 10 \%$ . The mass spectrometric determination of the  $CT_4^+ / CH_4^+$  ratio in samples diluted with a known volume of  $CH_4$  provided the most reliable data, giving an average yield of  $78 \pm 5 \%$ . From the substantial overlapping of such widely different methods, it was concluded that the average yield, based on the  $T_2$  activity, was around  $75 \%$ .

The radio gas chromatographic analysis, carried out with the molecular sieves column, indicated the remarkable radiochemical purity of the product, only a minor ( $0.5 \%$ ) impurity of  $T_2$  and/or HT being detected in the tritiated methane immediately after its purification. At the same time, the isotopic purity was also quite satisfactory, since the product contained over  $97.8 \text{ mol}\%$   $CT_4$ , with only traces of  $CHT_3$ ,  $CH_2T_2$  and  $CH_3T$ , as demonstrated independently by mass spectrometry and high-resolution gas chromatography.

Storage of  $CT_4$ . The high specific activity of  $CT_4$ , ca.  $1.17 \cdot 10^5$  Ci per mol, causes rapid self-radiolytic decomposition when the product is stored in the pure state, except perhaps at pressures below  $10^{-2}$  torr, where the absorption of the  $\beta$ -particles' energy by the gas is substantially reduced. However, the unreasonably large volume of the vessels necessary to store any significant amounts of  $CT_4$  at such low pressures, and the possibility of losses due to superficial adsorption, make this method highly unpractical. Storage in excess of A or Xe, sometimes reported (5,7), is only partially effective, owing to the extensive indirect radiolysis of  $CT_4$ . Dilution with a large ( $> 10^3 : 1$ ) excess of  $CH_4$  (2) effectively reduces the radiolytic formation of tritiated products other than methanes, such as HT,  $C_2H_3T$ ,  $C_2H_5T$ , etc. However, even at such large dilutions, a more subtle radiolytic effect, i.e. the intermolecular H/T scrambling leading to formation of partially tri-



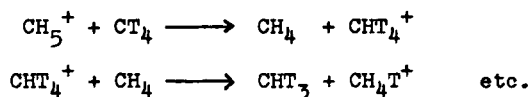
tiated methanes, was observed in the present investigation. Thus, the isotopic analysis of initially pure  $CT_4$ , diluted with  $CH_4$  to a molar ratio of  $1/1.15 \cdot 10^3$ , and stored for two weeks at  $20^\circ C$  and 760 torr in the presence of 2 mol%  $O_2$ , gave the following activity distribution:

$$CT_4 = 60.4 \% \quad CHT_3 = 29.4 \% \quad CH_2T_2 = 8.2 \% \quad CH_3T = 2.0 \%$$

corresponding to the isotopic composition:

$$CT_4 = 48.7 \text{ mol}\% \quad CHT_3 = 31.7 \text{ mol}\% \quad CH_2T_2 = 13.1 \text{ mol}\% \quad CH_3T = 6.5 \text{ mol}\%.$$

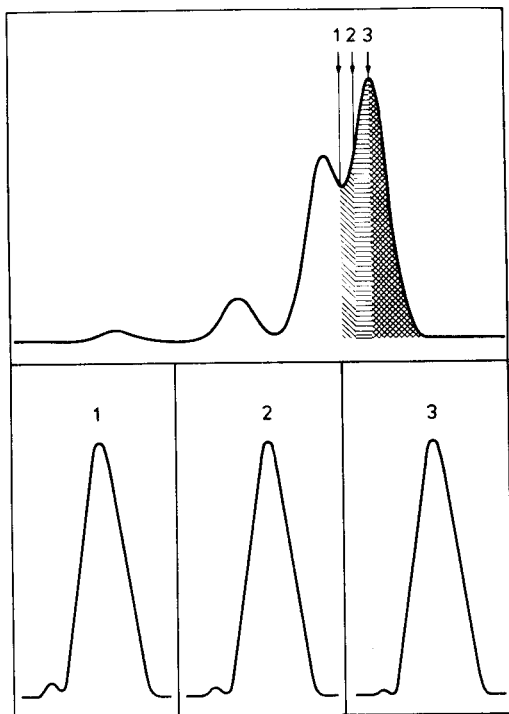
Both the rate of formation of  $CHT_3$ ,  $CH_2T_2$ , and  $CH_3T$ , and their relative yields, approaching the ratio 4 : 2 : 1, were typical of the chain isotopic exchange observed by Lawrence and Firestone to occur with high efficiency ( $G \approx 10^2$ ) in the radiolysis of  $CD_4/CH_4$  mixtures induced by tritium  $\beta$ -radiation (22), whose mechanism involves (22 - 24) a thermoneutral proton transfer from methonium ion to methane, e.g.:



Identification of the nature of the scrambling process allowed a dramatic improvement of the storage technique, based on the removal of the methonium ions, responsible of chain propagation, by an effective nucleophile, as ammonia (22). Indeed, it was found that addition of 1 - 2 mol%  $NH_3$ , without further dilution, completely suppressed the formation of the partially tritiated methanes, allowing the storage of reasonably diluted  $CT_4$  samples for extended periods of time.

Preparative gas chromatography. For applications requiring  $CT_4$  samples of the highest radiochemical and isotopic purity, a preparative gas chromatographic technique was developed, using the apparatus employed for the isotopic analysis, with the addition of a three-way stopcock, which allowed to introduce the effluent from

the column either into the flow counter, or into a short trap, packed with activated  $\text{SiO}_2$  and cooled with liquid nitrogen, which ensured excellent recovery of the eluted methane. The unusual preparative application of a capillary column was made possible by the fact that the activities of  $\text{CT}_4$  required for most experiments are contained in very small gas volumes: thus, injection of only  $2 \mu\text{l}$  of  $\text{CT}_4$  at  $20^\circ\text{C}$  and 760 torr allows purification of ca. 10 mCi of the product. Examples of preparative gas chromatography of an isotopically impure sample of  $\text{CT}_4$  are shown in Figure 3, which illustrates the isotopic composition of the recovered fractions, as measured by their subsequent analysis, as a function of the particular portion



**Figure 3:** Preparative gas chromatographic isolation of  $\text{CT}_4$  from an isotopically impure sample, showing the isotopic composition of recovered fractions as a function of the portion of the  $\text{CT}_4$  elution peak chosen for trapping.

of the elution peak of  $CT_4$  chosen for trapping. The results underline the high degree of purification achievable by preparative chromatography of  $CT_4$ . In this respect, it is worth pointing out that the small (< 0.5 %)  $CHT_3$  impurity invariably observed even in the best  $CT_4$  samples is likely to arise from radiolytic H/T scrambling occurring in the highly concentrated specimens during the time required for trapping and subsequent isotopic analysis.

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