

ISOTOPE ABUNDANCES IN CHLORINE

A STUDY OF ISOTOPE ABUNDANCES IN CHLORINE

by

WILLIAM JARVIS EDWARDS, B.Sc.

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AUTHOR: William Jarvis Edwards, B.Sc. (McMaster)

SUPERVISOR: Professor R. P. Graham

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SCOPE AND CONTENTS: A study of methods for determining the relative abundances of the chlorine isotopes, and the results of mass spectrometric analyses of several chlorine-containing substances. Small variations are shown to exist in nature between the relative abundances of the chlorine isotopes in halite samples from at least two different localities. Other studies involving chlorine isotopes and their possible fractionation are included.

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ABSTRACT

A good method has been devised for the mass spectrometric analysis of chlorine-containing substances by the use of dichlorotetrafluoroethane. A convenient preparation for this substance from chlorine and tetrafluoroethylene, obtained by the thermal decomposition of polytetrafluoroethylene ("Teflon"), has been developed.

Using dichlorotetrafluoroethane, and to a lesser extent, arsenic trichloride, chlorine isotope abundance data have been obtained for several chlorine-containing substances.

No evidence for isotopic fractionation has been found within either of two salt beds studied, but samples of halite from two different salt deposits have been found to differ in their relative abundance of chlorine isotopes by 0.5%.

There have been obtained indications of fractionation of chlorine isotopes in reactions involving the formation of chlorate from chloride and in the interaction of chlorate and chloride ions.

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GENERAL INTRODUCTION

The discovery by Richards (1) in 1914 that lead derived from the thorium disintegration series differed in atomic weight from that derived from the uranium series, led to acceptance of the view that an element formed by radioactive decay processes may show variations in isotopic abundance that are related to the source of the element. Shortly before, in 1912, Thomson (2) had built the first mass spectrometer and by means of it showed that some of the light elements consist of a mixture of isotopes. Later, Aston (3) and Dempster (4) measured the isotope abundances of a considerable number of elements by means of mass spectrometers. Variations in the isotope abundance ratios of the stable elements were not demonstrated, however, until 1934 when the first comprehensive survey of the isotopic constitution of hydrogen was published by Emeleus (5). Since this time such variations have been found for several elements, e.g., boron (6), carbon (7), oxygen (8), sulfur (9), and germanium (10).

The purpose of the present research is to develop a method for the mass spectrometric study of chlorine and to provide data concerning the isotope abundance ratio of chlorine derived from several naturally-occurring and synthetic chlorine-containing substances.

Although there has not yet been obtained experimental confirmation, it is interesting to note that the rather large variation of 0.031 atomic weight units has been predicted for the atomic weight of chlorine due to isotopic variations (11). Variation in the natural abundances of the chlorine isotopes would be of considerable importance, since it could effect not only the chemical atomic weight of chlorine, but also those of certain other elements, e.g. gold, whose atomic weights have been determined by reference to that of chlorine.

Theoretical variations in the atomic weight of chlorine can be calculated. For example, for the reaction,



Urey and Greiff (12) found an enrichment factor of 1.003 at 298.1°A. corresponding to 0.001 atomic weight units. Urey (11) calculated an equilibrium constant as large as 1.092 for the reaction



at 273.1°A.

Regarding such large enrichment factors and equilibrium constants, Urey states (11) that "The equilibrium constants for chlorine exchange reactions are surprisingly large. This is due to the increased number of vibrational degrees of freedom as the number of oxygen atoms combined with the chlorine atom increases, and the approximate constancy of the vibrational frequencies of all oxygen compounds of chlorine. Similar effects

should occur in the case of the sulfur isotopes, and in fact the experimental values for their fractionation between sulfur dioxide and bisulfite ion are close to the corresponding value of the chlorine isotopes". Recent calculations have been made for a number of isotopic equilibria involving the sulfur isotopes and some of the equilibria constants have been approximately verified (50).

While the foregoing shows the thermodynamic possibility of relatively large chlorine isotope fractionation comparable to that of sulfur, it has been shown with sulfur that large isotopic enrichment is often associated with various naturally-occurring oxidation and reduction cycles (13). Unlike sulfur, chlorine is little subject to plant or animal metabolic oxidation and reduction, and thus it may be that little fractionation of chlorine isotopes has taken place in nature due, as it were, to the lack of mechanisms by which equilibrium may be established. It is, therefore, of considerable interest to ascertain if possible whether atomic weight of chlorine does vary as much as one part in one thousand (11, 14).

HISTORICAL INTRODUCTION

A number of values have been reported in the literature for the abundance ratio of the isotopes of chlorine. Table I shows a compilation of such values.

TABLE I

ABUNDANCE RATIOS OF THE ISOTOPES OF CHLORINE

Investigator	Ref.	Isotopes Reported	Method of Investigation	Compound Analysed	Cl^{35}/Cl^{37} ratio
Aston	15	35,37,39	mass spectro-meter	HCl	3.00 to 3.10
Kallman and Lasareff	16	35,37,39	mass spectro-meter	HCl	3.24
Menzies	17	35,37	optical spectrometer	CCl	3.15
Nier and Hanson	18	35,37	mass spectro-meter	HCl	3.07 [±] 0.03
Graham, et al.	10	35,37	mass spectro-meter	GeCl ₄	3.000 [±] 0.003
Calculated using the atomic masses (19) of the Cl^{35} and Cl^{37} isotopes and the International Atomic Weight and the mass conversion factor (38).					3.103

As Table I shows, some investigators have reported the existence of a chlorine isotope of mass 39. Kallman and Lassareff (16) have reported the value of 6000/1 for the Cl^{35}/Cl^{39} ratio based on mass spectrometric data, and Meyer and

Levin (20) have claimed the detection of Cl^{39} in the absorption spectrum of hydrogen chloride. Similar work by Becker (21) and by Hettner and Bohme (22) appeared to confirm this. More recent work by Ashley and Jenkins (23) and by Hardy and Sutherland (24) failed, however, to confirm these earlier results. Nier and Hanson (18) were also unable to detect Cl^{39} . Recently Haslam, et al. (25) and Seaborg (26) have found Cl^{39} to be a radioactive substance capable of artificial production; its half-life is about one hour.

Although no mass spectrometric study of possible variation in the natural abundances of the chlorine isotopes has been reported, the earlier literature reveals numerous attempts to detect such variations by means of the small differences they would cause in the atomic weight of chlorine. It can be argued that the constancy of the atomic weight of chlorine as found by Stas and by Richards by various methods is due to the fact that all the samples of chlorine or chlorides used probably originated from sea-water chloride, which might reasonably be expected to have a constant isotopic abundance. In an attempt to avoid this difficulty Mlle. Curie (27) determined the atomic weight of chlorine in three minerals which were probably not of marine origin. For a sample of Canadian sodalite and Norwegian calcium chlorophosphate the atomic weights agreed with that of sea-water chloride. A higher value (35.60), however, was obtained for a sample of

sodium chloride from Central Africa. Following this, investigations by Gleditsch and Sandahl (28) and also by Dorenfeldt (29) using apatite from Odegaarden in Bamle, Norway, a substance presumably not of marine origin, showed no variation in the atomic weight of chlorine. Later attempts by Gleditsch (30, 48) in 1925 and 1927, Harkins and Stone (31, 32) in 1925 and 1926, and Menzies (33) in 1925 to find variation in the chemical atomic weight of chlorine were unsuccessful, although a considerable variety of chlorine-containing substances were examined.

THE OCCURRENCE OF CHLORINE IN NATURE

In general, naturally-occurring compounds and minerals of chlorine may be placed in one of three geological classifications.

(1) Igneous Rocks

These rocks are formed by the solidification of fused rock materials and include those of volcanic origin, where surface chlorides are often formed by the action of hydrogen chloride given off by active volcanoes.

(2) Metamorphic Rocks

These are rocks which have undergone some chemical or physical change following their original formation, as, for example, by the action of salt water flowing over various igneous rocks with resultant reaction between metal oxides and the aqueous chloride, to precipitate layers of an insoluble chloride such as that of silver or lead.

(3) Sedimentary Rocks

These are rocks formed by the precipitation of simple salts, as, for example, in the evaporation of a salt lake.

It has been possible to obtain a variety of mineral samples belonging to each of these classifications (Table II).

The present investigation, however, is concerned with those of the third class, which are the simplest chemically.

Table II lists only the naturally-occurring materials which were available for investigation in the present work; several other synthetic substances containing chlorine were also investigated (the term "synthetic" as used here refers to materials which have been either refined or synthesized by man) and will be described in the context.

TABLE II

NATURALLY-OCCURRING COMPOUNDS CONTAINING CHLORINE

CLASS	NAME	"FORMULA"	ORIGIN
IGNEOUS	Chlor-apatite	$(CaCl)Ca_4(PO_4)_3$	Snarum, Norway Espedalen, Norway
	Scapolite	$(Na, Ca)_4Al_3(Al, Si)_3Si_6O_4(Cl, CO_3, SO_4)$	Kingston, Ontario Templeton, Quebec Bolton, Massachusetts Grenville, Quebec Pargas, Finland
	Sodalite	$3NaAlSi_3O_8 \cdot NaCl$	Bancroft, Ontario Baikal, Siberia Vesuvius, Italy
	Sal Ammoniac	NH_4Cl	Paricutin, Mexico
	Lawrencite	$FeCl_2$	Meteoritic, Cañon Diablo, Arizona
METAMORPHIC	Carnallite	$KMgCl_3 \cdot 6H_2O$	Suria, Spain
	Pyromorphite	$PbCl_2 \cdot 3Pb_3(PO_4)_3$	Leadhills, Scotland Coeur d'Alene district, Idaho
	Percylite	$PbCl_2 \cdot CuO \cdot H_2O$	Chancay, Peru
	Hedyphane	$PbCl \cdot Pb_4(AsO_4)_3$	Langban, Sweden
	Vanadinite	$9PbO_3V_2O_5 \cdot PbCl$	Tucson, Arizona
	Eglestonite	Hg_4Cl_2O	Terlingua, Texas
	Terlinguaite	Hg_2ClO	Terlingua, Texas
	Calomel	Hg_2Cl_2	Terlingua, Texas
	Cerargyrite	$AgCl$	Bisbee, Arizona
	Embolite	$Ag(Br, Cl)$	Shafter, Texas
	SEDIMENTARY	Halite	$NaCl$
Halite in limestone		$NaCl$ in limestone	
Halite with Sylvite		$NaCl$ and KCl	Carlsbad, New Mexico

CHOICE OF A SUBSTANCE FOR MASS SPECTROMETRIC ANALYSIS

In order to be suitable for analysis in a gas-source mass spectrometer, an element or compound should have certain properties. In the present work the following criteria were used as a guide, and a search was undertaken for the chlorine-containing compound which would most adequately fulfil them.

- (1) The substance must be a gas, or at least must have an appreciable vapor pressure at room temperature.
- (2) The substance should be relatively simple in a molecular sense, in order to avoid a profusion of ion peaks which may complicate the interpretation of the mass spectrograms.
- (3) Elements other than chlorine in the substance should preferably be monoisotopic, and no ions of the same mass as those contributing the chlorine ion current should be capable of formation.
- (4) The substance should be capable of relatively easy synthesis in quantitative yields, and should lend itself to purification.
- (5) The substance must be stable and must not effect any part of the mass spectrometer unfavourably, e.g. it should have no corrosive properties, nor should it be so polar that it is easily sorbed in the instrument causing "memory effects".

EXPERIMENTAL

II Materials, Apparatus and Methodology

i. Reagents

Phosphorus Trichloride	B & A Reagent Grade
Arsenious Sulfide	A. D. MacKay
Mercurous Nitrate	B.D.H. "Analar"
Carbon Tetrachloride	Mallinckrodt (Purified)
Carbon Tetrabromide	Matheson
Carbon Tetraiodide	Prepared from ethyl iodide and carbon tetrachloride (41) Eastern Chem. Corp.
Ethyl Iodide	T. Baker Tech. (Anhydrous)
Aluminum Chloride	Mallinckrodt (Purified)
Carbon Disulfide	B & A Reagent
Sulfur Monochloride	Fisher (20 mesh course)
Iron	Mallinckrodt Analytical Reagent
Ferric Chloride	B & A reagent
Antimonic Chloride	Canadian Industries Ltd. from du pont de Nemours and Co.
Dichlorotetrafluoroethane	Frigidaire Limited, Toronto
Polytetrafluoroethylene	B.D.H. Certified Chemical
Potassium Permanganate	Canadian Industries Ltd. (C.P.)
Sulfuric Acid	Canadian Industries Ltd. (C.P.)
Hydrochloric Acid	Canadian Industries Ltd. (C.P.)
Nitric Acid	B & A Reagent
Lead Acetate	Eimer and Amend (C.P.)
Lead Nitrate	Nichols Reagent
Sodium Fluoride	B.D.H.
Phosphorus Pentoxide	Eimer and Amend (C.P.)
Dibutyl Phthalate	Canadian Liquid Air Co.
Nitrogen	

ii. Apparatus

The high vacuum apparatus used in the preparation of samples for mass spectrometric analysis is described in detail later, in the sections dealing with the compounds used. A brief description of the mass spectrometers used in the work follows.

(a) Mass Spectrometer No. 1.

This is a 90° direct-focussing gas-source mass spectrometer utilizing a three-plate Nier-type ion source (34). Ion current intensities are amplified by means of a linear inverse feedback d.c. amplifier which is coupled to a Leeds and Northrup Speedomax recorder. A detailed description of the instrument is given elsewhere (35). This mass spectrometer was used only for the analyses involving arsenic trichloride. The accelerating voltage was 1500 v. and the ionizing electrons were subjected to a potential of about 60 v.

(b) Mass Spectrometer No. 2.

This spectrometer is similar to Mass Spectrometer No. 1 except that it utilizes a four-plate "New Nier type" (36) ion source, and was previously designed for solid source work. The pyrex envelope of the mass spectrometer tube was, therefore, equipped with a 50/50 ground glass joint holding an electrically-heated tungsten filament. Solid material placed on this filament served as a source of thermions (37). In the present work the large opening in the ion source, through which the tungsten filament passed, was closed by means of an auxillary nichrome plate having a small opening (about 1/16th inch). The pyrex ground glass joint was replaced with a similar one holding a capillary leak which was connected to a

gas-handling system. The latter was a simplified version of the system used with Mass Spectrometer No. 1. Although the precision of this instrument was less than that of Mass Spectrometer No. 1 most of the data in this work were obtained on this instrument. The accelerating voltage was 1000-1200 and the ionizing electrons were subjected to a potential of about 40 v.

(c) Mass Spectrometer No. 3.

Mass Spectrometer No. 3 is a recently-constructed 90° instrument embodying similar electronic characteristics to Mass Spectrometers No. 1 and No. 2, but having an all-metal tube. (38). The tube is equipped with an interchangeable head, for solid or gas source work, which is bolted on and sealed by means of water-cooled "O" rings. The ion current is amplified and recorded by a system similar to that used with Mass Spectrometers No. 1 and No. 2. The instrument is fitted with adjustable collecting slits for simultaneous collection, if desired. The precision obtainable is similar to that of Mass Spectrometer No. 1. Several of the last analyses were carried out with this instrument. The accelerating voltage was 1500 v. and the ionizing electrons were subjected to a potential of about 60 v.

iii. Mass Spectrometer Procedure

The procedure in the mass spectrometric analyses was to analyse first an arbitrarily selected "standard sample" of the substance undergoing investigation, then an "unknown sample", and then the "standard" again, all under the same conditions. If the two analyses of the "standard" differed by more than would be expected from the precision of the results, instrumental "drift" was assumed to be occurring and the analyses were repeated at a later time. For the arsenic trichloride work, one of the "unknowns" was selected as the "standard", whereas for most of the dichlorotetrafluoroethane analyses the "standard" used was taken from a cylinder of the commercial product.

iv. Statistical Treatment of Results

Statistical methods were developed for the comparison of an "unknown" with a "standard" sample, and also for the comparison of one "unknown" sample with another. In the latter case the statistical method was developed for the particular situation where the two unknowns had each been analysed twice, with reference to the "standard". The methods take into account the shift in the values of the analyses caused by day to day variation of the instrument. The use of these methods makes possible the assignment of a probability that a given difference

in isotope abundance ratios results only from chance statistical variation. The mathematical derivations of the methods are given in Appendix I and Appendix II.

II Study of Various Compounds of Chlorine

Several compounds were studied with respect to their possible use as ion sources in a mass spectrometer. Previous work (39) with chlorine and hydrogen chloride has shown that these substances are unsatisfactory; the former because of its corrosive properties particularly with respect to mercury, and the latter because its highly polar nature leads to "memory effects" in the mass spectrometer. Four other volatile compounds of chlorine were studied in some detail, namely: phosphorus trichloride, arsenic trichloride, carbon tetrachloride, and dichlorotetrafluoroethane. The results of these investigations are very briefly summarized below.

i. Phosphorus trichloride

This compound was tested mass spectrometrically using B & A Reagent Grade chemical after redistilling it in vacuo, and it showed some promise as an ion source. The compound was not considered suitable, however, because of its pronounced tendency to hydrolyse to hydrogen chloride and the difficulty of preparing it quantitatively from the sources of chlorine which it was desired to study.

ii. Arsenic trichloride

A method of synthesis for this compound was developed, which gave good yields of a very pure product. The method, which is given in detail later, consisted of the reaction of a heavy metal chloride with arsenious sulfide under high vacuum. Although mass spectrometric analyses using this compound were obtained, it was necessary to discontinue work with this substance when it was found to be reacting with the stopcock grease in the gas-handling system of the mass spectrometer. This reaction caused contamination of the instrument.

iii. Carbon tetrachloride

This substance has previously been analysed mass spectrometrically (40), and in the present work experiments confirmed that it is a satisfactory ion source. Several procedures were studied in an attempt to find a suitable means of synthesizing it quantitatively.

To this end, carbon disulfide was chlorinated using sulfur monochloride, under reflux, with, as catalysts, iron, antimony, ferric chloride, and antimonie chloride. With reaction times up to three days, yields of only 45 to 75% were obtained.

The chlorination of other halogenated methanes such as carbon tetraiodide and carbon tetrabromide was also attempted using chlorine and sulfur monochloride and the previously-

mentioned catalysts. Except in the case of chlorine and carbon tetrabromide, reaction visibly occurred but carbon tetrachloride could not be isolated from the reaction products.

A very substantial amount of work was devoted to synthetic methods for carbon tetrachloride, because of its promise as a suitable substance for chlorine isotope abundance studies. The lack of success in finding a suitable synthetic method, however, eventually caused the reluctant abandonment of this compound.

iv. Dichlorotetrafluoroethane

This compound proved to be a very efficient source of ions, and a very satisfactory material to handle in a mass spectrometer and to synthesize. A simple method of preparation, which is described later, has been developed, and most of the isotope abundance results in this work were obtained using this compound.

III Arsenic Trichloride

i. Preparation

The preparation of arsenic trichloride can be accomplished in several ways (42) but in the present work the reaction of a heavy metal chloride with arsenious sulfide was chosen because of the ease with which it may be carried out in a vacuum system. Mercurous chloride was chosen as the heavy metal chloride because it is easily prepared from the soluble chloride

starting materials by precipitation, is not hygroscopic, and can be stored without decomposition. Silver chloride was also examined but did not seem as satisfactory in the reaction; also, it is subject to photolysis.

The overall reaction is represented by:



(a) Procedure for Arsenic Trichloride

Pure, dry, finely-powdered arsenious sulfide is dried in an electric oven at 150°C. for two hours before use.

Mercurous chloride is prepared by precipitation from a solution of a chloride whose isotope abundance it is desired to study, using a 0.5 M solution of mercurous nitrate in about 5% excess of the stoichiometric requirement. The precipitate is filtered by vacuum through ordinary "Cenco" filter paper, or any similar filter paper that is sufficiently hard. Hardness in the filter paper is desirable in order that the precipitate will remain on the surface rather than penetrate deeply into the paper. After filtration, the filter paper is removed from the funnel and the residue removed from the paper with a clean spatula and placed on a watch glass. The paper with a small amount of residue remaining is placed on another watch glass. Both watch glass are then placed in an oven at 110 - 115°C. for 15 minutes, after which time the filter paper should be quite dry but not discoloured. In this state the last trace of mercurous chloride may be removed from it in the form of brittle chips, by simply flexing the paper. The

main portion of the mercurous chloride, together with that removed from the dried filter paper, are then placed in a pyrex glass mortar and ground to a fine powder. This powder is placed on one of the watch glasses used previously and replaced in the oven for two hours at 110°C . to remove the last traces of moisture.

The dry arsenious sulfide and mercurous chloride are then intimately mixed, using arsenious sulfide in about 20% excess of the stoichiometric proportion, and placed on the vacuum line (Figure 1) in the reaction bulb (R-B). The mixture, after evacuation of the line to a pressure of about 10^{-4} mm. is heated gently with a "brush" flame using a hand torch. After generation of the volatile arsenic trichloride a black residue remains in the bulb and a yellow deposit is formed around the neck of the bulb. These are, presumably, mercurous sulfide and sublimed arsenious sulfide, respectively.

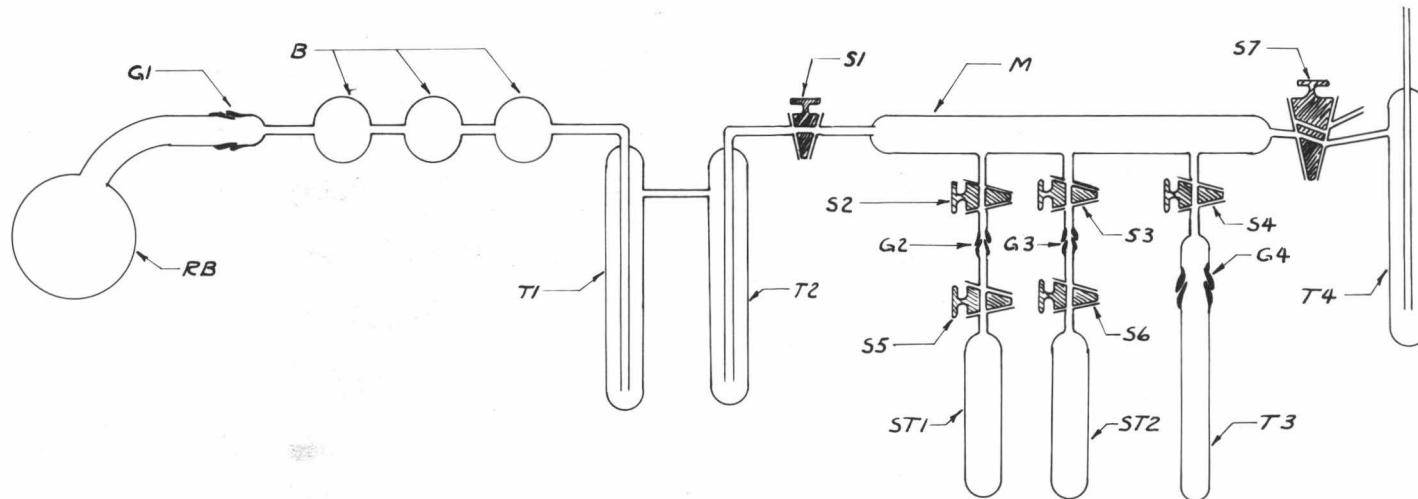
After the sample has passed through glass wool (B) to remove traces of solids, it is collected in trap (T-1) by means of liquid air. A bright metallic mirror is often formed on the sides of this trap, probably due to arsenic or mercury.

The sample is distilled slowly to trap (T-2) by replacing the liquid air on trap (T-1) with an ice and salt bath (approx. -15°C .) and placing a liquid air bath on trap (T-2). The liquid air bath on trap (T-2) is then replaced by a dry ice and ethanol bath (approx. -78°C .) and a liquid air bath placed on trap (T-4) and the sample of arsenic trichloride is subjected to the

LEGEND FOR FIGURE 1

- B Glass bulbs filled with pyrex glass wool
- G 1 Ground glass joint, standard taper, 10/30
- G 2 Ground glass joint, standard taper, 10/20
- G 3 same as G 2
- G 4 same as G 1
- M manifold
- T 1 Condensation trap
- T 2 Condensation trap
- T 3 Drying trap, contains magnesium sulphate
- T 4 Condensation trap
- S 1 High vacuum hollow plug stopcock, 4 mm. bore
- S 2,3,4, High vacuum hollow plug stopcocks, 3 mm. bore
- S 5,6 Stopcocks, solid plug, 2 mm. bore
- S 7 High vacuum hollow plug stopcock, double transverse, 3 mm. bore
- RB Reaction bulb, approximately 4 cm. diameter

(a high vacuum pumping system consisting of a single stage mercury condensation pump backed by a Welch "Duo Seal" forepump is connected at trap T-4)



APPARATUS FOR THE PREPARATION
OF ARSENIC TRICHLORIDE

action of the vacuum pumps for 20 minutes to remove substances volatile at dry ice temperatures, e.g., air, hydrogen chloride. Non-condensable materials are conveyed through the vacuum pumps and other materials are caught in trap (T-4). Stopcock (S-7) is shut off and the arsenic trichloride distilled from trap (T-2), after removal of the dry ice bath, to the drying tube (T-3) where it is collected by means of a liquid air bath. With stopcock (S-4) closed the sample is allowed to stand at room temperature in contact with magnesium sulfate, as a drying agent, for two to four hours. With stopcocks (S-1) and (S-7) closed the sample is then collected in a sample tube (ST-1) or ST-2) by means of a liquid air bath.

11. Results with Arsenic Trichloride

Two results only were obtained using arsenic trichloride as a substance for mass spectrometric analysis before work with this compound was halted for the reasons indicated earlier. The two samples studied were prepared from sodium chloride from the Elk Point, Alberta salt beds. These samples are each from the Elk Point #2 shaft, but taken from different levels. The results are shown in Table III and are calculated from the ion peaks corresponding to masses 180 and 182 assuming a binomial distribution of chlorine atoms.

TABLE III
ISOTOPE ABUNDANCE DATA
OBTAINED USING ARSENIC TRICHLORIDE

<u>Starting Material</u>	<u>Source</u>	<u>Cl³⁵/Cl³⁷ ratio</u>	<u>Standard Deviation x10³</u>	<u>No. of Spectrograms</u>
Halite	Elk Pt. #2 mine 2800 ft. level	3.094	3.5	7
Halite	Elk Pt. #2, mine 4000 ft. level	3.095	3.8	8
Halite	Elk Pt. #2 mine 2800 ft. level	3.096	3.6	8

IV Dichlorotetrafluoroethane

1. Preparation

The preparation of dichlorotetrafluoroethane that was used consists of three stages: the preparation of tetrafluoroethylene, the preparation of chlorine, and the combination of these to give dichlorotetrafluoroethane.

The preparation of chlorine was accomplished by the common method of allowing a solution of a chloride to react with excess potassium permanganate and sulphuric acid, and is not given in detail here. Several methods of preparation of tetrafluoroethylene are available (43,44,45). The thermal degradation of the commercial polymer "Teflon" (polytetrafluoroethylene) in vacuo was selected because of its convenience.

(a) Procedure for Tetrafluoroethylene

The vacuum system used in this procedure and in the preparation of the dichlorotetrafluoroethane is shown in Figure 2.

Three to six grams of polyterafluoroethylene are tightly packed into a porcelain boat (approximately $3 \times \frac{1}{2} \times \frac{1}{2}$ ", not shown); the amount being chosen so that the amount of tetrafluoroethylene produced will be in about 10 to 20% excess over the theoretical amount of chlorine to be prepared. The boat containing the "Teflon" is placed in the "Vycor" furnace tube (F-T) by removing the ground glass joint (G-1) and then replacing it after lubrication with Apiezon N high vacuum grease. (All ground glass joints and stopcocks are lubricated with Apiezon N excepting (S-5), (S-7), and (S-8) which are lubricated with Dow Silicone high vacuum grease). Stopcock (S-1) is opened and stopcock (S-2) and (S-4) are closed and stopcock (S-3) set to connect the manifold (M) with tube (C) leading to the collection system. Stopcock (S-5) is set to connect all three lines leading to it, and stopcock (S-7) is closed to all connections. Following this, stopcock (S-6) is opened to the high vacuum pumps and the system is evacuated to a pressure at least as low as 10^{-3} mm.

The compressed air line (A) is turned on to cool the greased joints of the furnace tube (F-T) and trap (T-1) is cooled with liquid air. The electric furnace (E-F) is then turned on

and the temperature (measured by a thermocouple, not illustrated, within the furnace beside the furnace tube) is raised to 450 to 600°C. The pyrolysis products are frozen as a white powder in trap (T-1) by means of the liquid air. After 30 to 40 minutes the furnace is turned off and allowed to cool. Stopcock (S-3) is closed and stopcock (S-5) set to connect trap (T-1) and reaction bulb (RB). The liquid air is then removed from trap (T-1) and the product it contains permitted to warm up.

The yield is calculated from the pressure read on the manometer (Z) and the volume of the system now containing the gas (3.80 ± 0.05 liters), assuming the ideal gas laws and that the only product is tetrafluoroethylene. On this basis yields are 93 ± 2%. The product is then frozen into trap (T-1) by means of a liquid-air bath and then stopcock (S-5) is set to close all three lines leading to it.

(b) Procedure for Dichlorotetrafluoroethane

Chlorine is prepared by the reaction of a saturated solution of a chloride together with a large excess of potassium permanganate to which a 50% sulphuric acid solution is added slowly so as to control the rate of evolution of gas. The system is swept continuously with nitrogen and the exit gases passed through a drying bottle containing sulfuric acid and then through stopcock (S-8), in Figure 2, into trap (T-7). The chlorine is liquefied here by means of a dry-ice and alcohol bath and the nitrogen is allowed to escape through stopcock (S-7) which is set

to connect trap (T-7) to the atmosphere. Heat from a "brush" flame is used to ensure complete evolution of chlorine. The sweeping with nitrogen is then discontinued, stopcock (S-8) closed and stopcock (S-7) set to connect trap (T-7) to the reaction bulb (RB). The dry ice is removed from trap (T-7) and after the chlorine has evaporated and warmed to room temperature the yield is measured as in the case of tetrafluoroethylene. Yields of $95 \pm 3\%$ are obtained. Allowance is made for 1.4 cm. pressure caused by nitrogen remaining in trap (T-7); this value was determined by a blank run. Stopcock (S-5) is then set to connect reaction bulb (RB) and trap (T-1) and the chlorine caused to freeze, with the tetrafluoroethylene stored there, by means of the liquid-air bath. Nitrogen and any other non-condensable material is removed by the vacuum pumps through stopcocks (S-3), (S-2) and (S-6), and then stopcock (S-3) is closed. The liquid air is removed from trap (T-1) and the chlorine and tetrafluoroethylene allowed to volatilize into the reaction bulb (RB). (If the chlorine and tetrafluoroethylene are allowed to mix at room temperature the reaction is too violent and the mixture will burst into flame.) Two hours are allowed to ensure complete reaction which is substantially quantitative. The products are then frozen in trap (T-4), by means of liquid air, through stopcocks (S-5), (S-2), (S-3) and (S-9), stopcocks (S-6) and (S-10) being closed. By transferring the liquid-air bath between traps (T-3) and (T-4) and manipulating stopcocks (S-9)

LEGEND FOR FIGURE 2

- A Compressed air line to cool joints at the end of F T
- B 6 inch squares of asbestos to stop radiation from furnace (E F)
- C, D 8 mm. pyrex tubes
- E F electric furnace
- F T "Vycor" furnace tube for pyrolysis
- M manifold
- G,1,2 ground glass joints, male of "Vycor", female of pyrex, standard taper, 24/40
- G 3,4 ground glass joints, standard taper, 24/40
- S 1,2,4,8 high vacuum stopcocks, hollow plug, mm. bore
- S 3,7 high vacuum stopcocks, hollow plug, double transverse 3 mm. bore
- S 5 high vacuum stopcock, hollow plug, right-angled 2 mm. bore
- T 1,2,3,4 condensation traps
- T 5 trap containing sodium hydroxide pellets
- T 6 removable condensation trap
- T 7 spiral condensation trap for collection of chlorine
- R B reaction bulb approximately 3.5 liters capacity
- D T Drying trap, 250 ml. bulb containing phosphorus pentoxide on pyrex glass wool
- Z 80 cm. direct-reading manometer: the mercury is covered with 1/8 inch of dibutyl phthalate

(A high vacuum system consisting of a single stage mercury condensation pump and a Welch "Duo Seal" forepump is connected to (S-6).

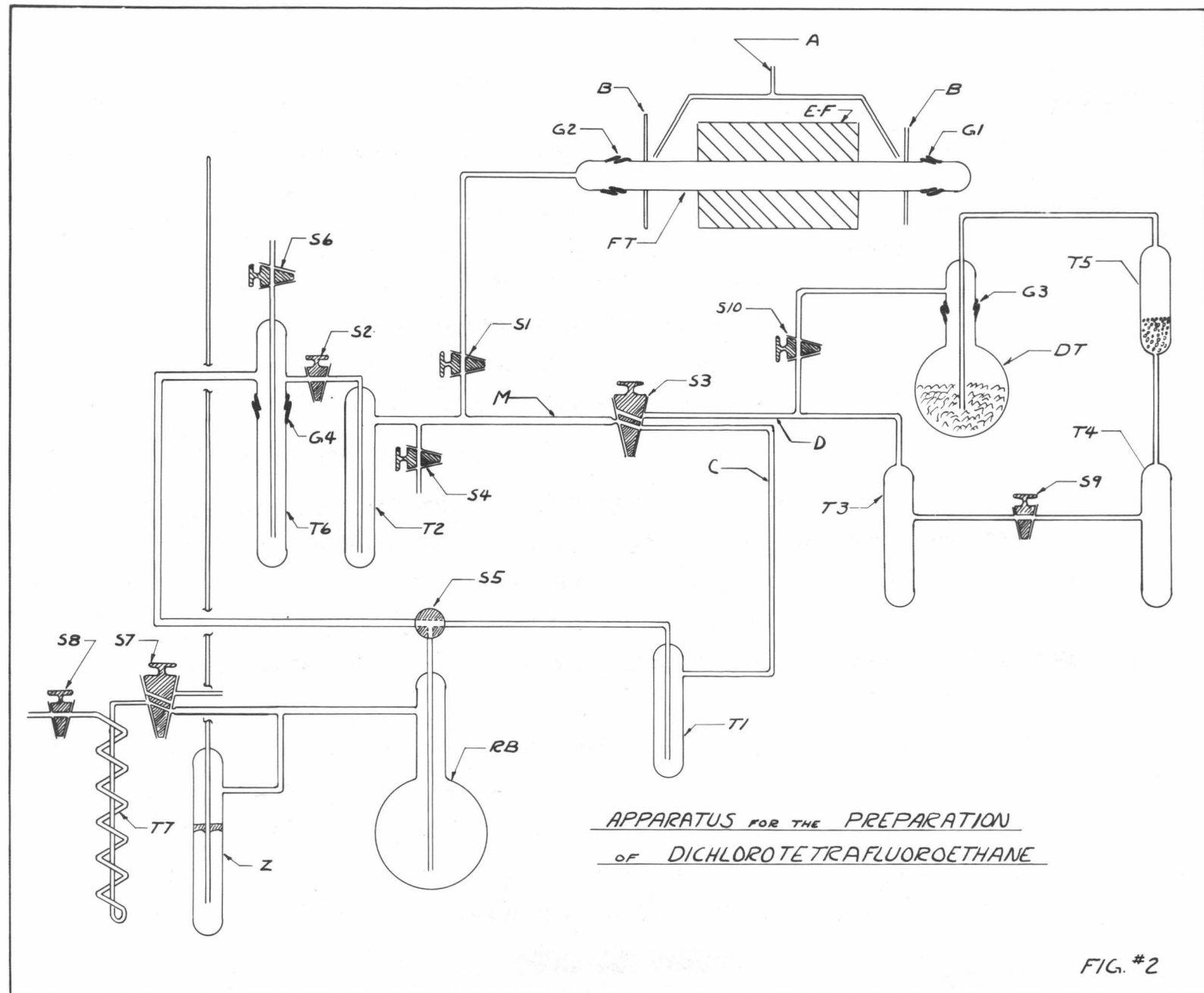


FIG. #2

and (S-10), after closing stopcock (S-3), the material is passed several times through trap (T-5), containing sodium hydroxide pellets, to remove hydrogen chloride and through the drying trap (D-T), containing phosphorus pentoxide on glass wool, to remove water. The material is then collected in trap (T-3) by means of the liquid-air bath and stopcocks (S-9) and (S-10) are closed. A liquid air bath is placed on trap (T-4) and a dry ice and alcohol bath on trap (T-3) and stopcock (S-9) opened for about 10 minutes. Dichlorotetrafluoroethane does not distil at an appreciable rate between these two temperatures (-78° and -180°C . approximately) but the excess tetrafluoroethylene is rapidly distilled into trap (T-4), from whence it is later discarded. Stopcock (S-9) is then closed and the dichlorotetrafluoroethane in trap (T-3) is distilled through stopcock (S-3) into a sample tube* attached to the manifold (M) by means of a liquid air bath on the sample tube. Stopcocks (S-4), (S-1) and (S-2) are closed during this procedure. The sample tube is then removed from the manifold by fusing its capillary connection, using an oxygen torch. (Yield $97\pm 3\%$)

ii. Mass Spectrum of Dichlorotetrafluoroethane

The mass spectrometric analysis of dichlorotetrafluoroethane for the measurement of the $\text{Cl}^{35}/\text{Cl}^{37}$ ratio was carried out in the 130-140 mass range by measuring the ion currents

* See Fig. 1b, ref. 10.

at mass numbers 135 and 137, corresponding to the ions $C_2^{12}F_4Cl^{35+}$ and $C_2^{12}F_4Cl^{37+}$. Small ion currents were observed corresponding to mass numbers 136 and 138 which could be largely accounted for as $C^{12}Cl^{13}$ isotopic modifications of the preceding assuming that C^{13} is present to the extent of 1%. A small fraction of these ion currents at mass number 136 and 138 may also have been caused by $C_2^{12}F_4HCl^{35+}$ and $C_2^{12}F_4HCl^{37+}$ ions.

In addition to the above, ion currents corresponding to all the singly-charged ions which can be formed from dichlorotetrafluoroethane, $Cl-C-C-Cl$, and 1, 2,-dichloroperfluoropropane, CF_3-C-CF_2 , (perfluoropropene, $CF_3-CF=CF_2$, is also formed in the pyrolysis of "Teflon") were observed.

Three other "anomalous" ion currents were observed, corresponding to mass numbers 101, 103, and 105. These ion currents were interpreted as being due to $C^{12}FCl_2^{35+}$, $C^{12}FCl^{35}Cl^{37+}$, and $C^{12}FCl_2^{37+}$ respectively, in a proportion of about 10% relative to the $C^{12}F_2Cl^+$ ions formed by cleavage of the carbon to carbon bond of dichlorotetrafluoroethane. As the addition of chlorine across a double bond cannot give rise to two chlorine atoms attached to the same carbon atom, the possibility arises that the "Teflon" may contain some carbon to chlorine linkages and give rise to, for example, perfluorovinylchloride, $CF_2=CFCl$, along with the tetrafluoroethylene monomer, $CF_2=CF_2$. Addition of chlorine

to perfluorovinylchloride would then yield 1,1,2-trichloro-
perfluoroethane, $\text{Cl}-\overset{\text{F}}{\underset{\text{ClF}}{\text{C}}}-\overset{\text{F}}{\text{C}}-\text{Cl}$, with two chlorine atoms attached
to the same carbon atom. Alternatively, the "Teflon" may
contain some carbon to hydrogen bonds which, after the forma-
tion of the monomer and addition of chlorine, could undergo
substitution by chlorine to yield 1,1,2-trichloroperfluoro-
ethane. Cleavage of this substance could yield CFCl_2^+ ions.

In an effort to throw light on this question, an
analysis of the "Teflon" was undertaken. The material was
fused with sodium by the procedure of Shriner and Fuson (46)
and a gravimetric fluoride analysis (47) performed in order to
calculate the efficiency of the fusion. The chloride was then
determined nephelometrically and a blank chloride analysis
carried out with the sodium (which very likely had been prepared
by the electrolysis of fused sodium chloride).

The chloride found in the "Teflon" analyses could be
entirely accounted for by the trace amounts found in the sodium
blank. By considering the limits of the experimental error of
the method, an upper limit for the chlorine concentration in
the "Teflon" can be set at 0.09%.

As it does not seem reasonable that a chlorine con-
centration of less than 0.09% in the "Teflon" could account for
the concentration of CFCl_2^+ ions observed, and as other evidence
indicates that both hydrogen and chlorine are absent (49), it is
suggested that perhaps some triply-unsaturated compounds or free
radicals may be formed from "end groups" in the polytetrafluoro-
ethylene molecules.

iii. Results with Dichlorotetrafluoroethane

(a) Naturally-occurring Compounds of Chlorine

Table IV shows the sample designations assigned to the samples of dichlorotetrafluoroethane prepared from the chlorine-containing minerals studied. Table V shows the mass spectrometric results obtained from the analyses of these samples. In some cases analyses were repeated (see Analysis No., Table V) due to a drift in the value of the "standard" or in an attempt to improve the precision of the results. Most of the analyses were done in the form of "standard, unknown, standard", previously described. Sample A and Sample B were prepared from the same material as Sample 8 and Sample 2, respectively, but compared directly against one another on Mass Spectrometer No. 3, to verify the results obtained when Samples 2 and 8 were analysed separately against the same "standard" on Mass Spectrometer No. 2. The analyses using Mass Spectrometer 3 were carried out by Mr. W. H. Fleming, M.Sc., and Mr. T. Kennett.

TABLE IV
NATURALLY-OCCURRING CHLORIDES AND
CORRESPONDING DICHLOROTETRAFLUOROETHANE SAMPLES

<u>Origin of Chlorine</u>	<u>Source of Mineral</u>	<u>Dichlorotetrafluoroethane Sample Designation</u>
Halite	Detroit, Michigan	2 and B
Carnallite	Suria, Spain	4
Halite	Stassfurt, Germany	6
Halite	Avery Island, Louisiana, 520 ft. depth	8 and A
Halite	Ibid, 15 ft. depth	9

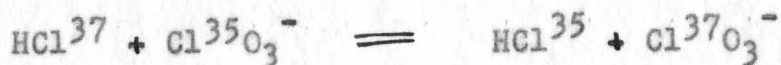
TABLE V

ISOTOPE ABUNDANCE RATIOS OF NATURALLY-OCCURRING CHLORIDES

Sample No.	Analysis No.	Mass Spec. No.	Material Used as standard	Cl ³⁵ /Cl ³⁷ ratios of bracketing standards	No. of spectrograms contributing to standards	Mean Cl ³⁵ /Cl ³⁷ ratio of standard	St. Dev. of standard x 10 ⁺³	Cl ³⁵ /Cl ³⁷ ratio of unknown sample	St. Dev. of unknown sample x 10 ⁺³	No. of spectrograms contributing to unknown sample	Difference in isotope abundance ratio between unknown and standard
2	1	2	cylinder	3.097 3.121	8 8	3.109	8.6*	3.123	13.6	8	+0.014
2	2	2	of	3.102 3.110	9 8	3.106	12.1	3.116	8.4	7	+0.010
4	1	2	com- mercial	3.109 3.103	8 8	3.106	7.7	3.108	4.1	8	+0.002
6	1	2	dichloro-	3.113 3.111	8 11	3.112	9.9	3.109	7.0	8	-0.003
8	1	2	tetra-	3.108 3.105	9 8	3.107	10.8	3.091	13.1	8	-0.016
8	2	2	fluoro-	3.103 3.105	8 8	3.104	7.0	3.097	12.6	11	-0.007
9	1	2	ethane	3.109 3.101	8 9	3.105	9.0	3.093	9.8	7	-0.012
B	-	3	Sample A	3.091 3.076	8 8	3.084	7.1	3.103	3.0	8	+0.019
A	-	3	Sample B	3.094 3.094	8 8	3.094	4.7	3.082	3.1	7	-0.012

(b) Synthetic Materials Containing Chlorine

Some attention was given to the possibility of bringing about the exchange of chlorine isotopes in the laboratory. Urey (11) has calculated the equilibrium constants for a number of exchange reactions, and found a value of 1.043 for K for the reaction



at 298.1°A.

As an equilibrium constant of this magnitude would create easily-detectable changes in isotope abundance ratio, an attempt was made to set up an equilibrium for which the equilibrium constant should be similar, namely,



and to measure possible changes in the isotope abundance ratio.

Several grams of potassium chlorate were heated with an equal weight of manganese dioxide in a "Vycor" crucible in a blast flame for two hours in order to decompose the chlorate quantitatively to potassium chloride by the reaction



The contents of the crucible were then boiled with 250 ml. of water to dissolve the potassium chloride and then filtered by vacuum to remove the manganese dioxide. The filtrate was then evaporated to dryness and dichlorotetrafluoroethane prepared from the potassium chloride that was recovered. This dichlorotetrafluoroethane was labelled Sample 3, and

analysed mass spectrometrically. The results are shown in Table VI. Since the decomposition reaction is quantitative, the potassium chloride formed should have the same chlorine isotope abundance ratio as the original potassium chlorate.

Following this, two solutions were made up as follows: potassium chloride was prepared from potassium chlorate (as above) and placed in solution with an approximately equivalent weight of the potassium chlorate. The solutions were placed in a water bath at 25°C. Some sulfuric acid was added to one of the solutions as it was considered that the rate of exchange might be dependent on the pH.

No. 1 solution contained:

3.13 gm. potassium chloride
5.17 gm. potassium chlorate
in 200 ml. of water

No. 2 solution contained:

2.2501 gm. potassium chloride
3.7694 gm. potassium chlorate
0.55 ml. sulfuric acid (18 M)
in 200 ml. of water

After nineteen days Solution No. 1 was removed from the water bath. The solution was acidified with three drops of 18M sulfuric acid to prevent the formation of silver oxide, and most of the chloride precipitated by the addition of 370 ml. of 0.1001 N silver nitrate solution. The precipitated silver chloride was removed by vacuum filtration, and the filtrate made neutral to phenolphthalein by means of 0.1 N sodium hydroxide solution, and then evaporated to dryness. A considerable

amount of crystalline material had formed at this stage, which adhered tenaciously to the beaker in which the evaporation was carried out. Mixed salts to a weight of 7.95 grams were removed from the beaker (theoretical, about 9.3) and this mixture was then heated with manganese dioxide to convert the potassium chlorate to chloride, and dichlorotetrafluoroethane prepared from it in the manner described previously. This sample was labelled as Sample No. 5 and analysed mass spectrometrically (Table VI).

The precipitation of the chloride in Solution No. 1 was not quantitative as theoretically 0.38 gm. of potassium chloride should remain with the 5.17 gm. of potassium chlorate. Some concern, felt at the time, over the possibility of formation of the explosive silver perchlorate if an excess of silver nitrate were used, was the reason for this.

Solution No. 2 was removed from the water bath after sixteen days and the chloride precipitated quantitatively by using a solution of 5.1262 gm. of silver nitrate in 200 ml. of water. The solution was neutralized and evaporated to dryness in the same manner as Solution No. 1. Mixed salts weighing 7.8266 grams were recovered from the beaker used in the evaporation (theoretical, about 8.5 gm.). After treatment with manganese dioxide and heat and conversion to dichlorotetrafluoroethane, the dichlorotetrafluoroethane was labelled Sample 7 and analysed mass spectrometrically. The results are shown in Table VI.

In addition to the mass spectrometric results for

dichlorotetrafluoroethane Samples 3, 5, and 7, Table VI also includes the results of two other dichlorotetrafluoroethane samples, Samples 10 and 11. These samples were compared directly, with Sample 10 serving as "standard". The materials from which they were prepared were:

- Sample 10 prepared from refined sodium chloride obtained from the Electric Reduction Co., Brickingham, P.C.
- Sample 11 prepared from sodium chlorate which in turn had been prepared by electrolysis of the above-mentioned sodium chloride, by the Electric Reduction Co.

TABLE VI

ISOTOPE ABUNDANCE RATIOS OF SYNTHETIC CHLORINE-CONTAINING MATERIALS

Sample No.	Analysis No.	Mass Spec. No.	Material used as standard	Cl ³⁵ /Cl ³⁷ ratios of bracketing standards	No. of Spectrograms contributing to standards	Mean Cl ³⁵ /Cl ³⁷ ratio of standard	St.Dev. of standard x 10 ³	Cl ³⁵ /Cl ³⁷ ratio of unknown sample	St. Dev. of unknown sample x 10 ³	No. of spectrograms contributing to unknown sample	Difference isotope abundance ratio between unknown and standard
3	1	2	Dichloro-	3.099 3.111	7 7	3.105	9.3	3.117	6.5	7	+0.012
3	2	2	tetra-	3.106 3.102	9 9	3.104	9.2	3.125	5.0	8	+0.021
5	1	2	fluoro-	3.111 3.095	8 8	3.103	6.9	3.113	5.7	8	+0.010
5	2	2	ethane	3.098 3.095	7 7	3.097	8.9	3.108	7.0	8	+0.011
7	1	2	from	3.108 3.118	7 5	3.113	8.8	3.106	6.1	7	-0.007
7	2	2	cylinder	3.113 3.110	8 8	3.112	7.6	3.100	11.9	8	-0.012
11	1	3	Dichloro-tetrafluoro	3.093 3.095	8 8	3.094	5.9	3.098	11.5	8	+0.004
11	2	3	ethane Sample No. 10	3.088 3.088	8 8	3.088	8.9	3.093	9.4	8	+0.005

DISCUSSION

i. Arsenic Trichloride

No significant differences were found in the abundance ratios of the isotopes of chlorine in samples of halite from two levels of the same salt bed (Table III). This may be accounted for in three ways, viz.,

(1) No preferential solubility between the two isotopic salts of sodium chloride exists that is large enough to cause a detectable variation in isotope abundance. This assumes that the salt bed was deposited by the continuous evaporation of a salt lake.

(2) The salt bed was deposited by periodic evaporation of a salt lake with isotope fractionation taking place, but the two samples studied came from equivalent "isotopic positions" within two layers.

(3) Preferential solubility may exist between the isotopic modifications of sodium chloride, but the salt bed may have been laid down under non-equilibrium conditions.

In the writer's opinion the first explanation seems the most reasonable. Experimental results which are discussed later tend to confirm this explanation.

ii. Dichlorotetrafluoroethane

The analysis of the "Teflon" used shows that if any chlorine is present in this material, its concentration is less

than 0.09%. Subsequent to the carrying out of these analyses, the producer (du Pont de Nemours and Co.) has advised that "the impurities in "Teflon", if any, are in the parts per million level". In view of this it seems reasonable to conclude that substantially all the chlorine in the $C_2F_4Cl^+$ ion peaks that were measured, corresponding to the mass numbers 135 and 137, came from the mineral and that the "anomalous" $CFCl_2^+$ ions are not due to "foreign" chlorine. In regard to the influence of molecular species other than dichlorotetrafluoroethane on the accuracy of the relative abundance determinations, it may be noted that no molecular species of chlorofluoro-substituted hydrocarbon with two chlorine atoms attached to the same carbon atom can yield singly-charged ions of mass numbers 135 and 137 except, possibly, by recombination of ions within the mass spectrometer. Further, differences in isotope abundance ratios obtained with two samples of dichlorotetrafluoroethane prepared from different sources of chlorine, are quite reproducible when the preparations are repeated and the material analysed on a different mass spectrometer by a different operator.

(a). Naturally-occurring Compounds of Chlorine

As can be seen from Table V, several of the isotope abundance ratios for the "unknown" samples" differ considerably from the mean isotope abundance ratio of their bracketting

"standards". Table VII shows the probabilities that these differences are due only to chance instrumental conditions (see Appendix I).

TABLE VII

PROBABILITY THAT "UNKNOWN DICHLOROTETRAFLUOROETHANE DOES NOT DIFFER IN ISOTOPE ABUNDANCE RATIO FROM THAT OF "STANDARD"

Unknown Sample	Difference in isotope ratio from standard	Probability that the difference is due to chance	Analysis No.
2	+0.014	0.002	1
2	+0.010	0.023	2
4	+0.002	0.483	1
6	-0.003	0.289	1
8	-0.016	0.001	1
8	-0.007	0.065	2
9	-0.012	0.004	1
B	+0.019 Sample A as "standard"	not calculated	
A	-0.012 Sample B as "standard"	not calculated	

Consideration of the "unknown samples" with respect to each other is perhaps of more interest than with respect to the arbitrarily selected "standard". In this connection it is of interest to note that the average isotope abundance ratio of the two analyses of Sample 8 and the isotope abundance ratio of Sample 9 differ from the standard by the same amount. As these

two samples come from the same salt bed at different levels the results may be considered as confirmation of those obtained using samples from the Elk Point No. 2 mine (see Table III) where no difference in isotope abundance ratio with depth was found.

The largest difference in isotope abundance ratio between naturally-occurring materials was found between Samples 2 and 8 (and 9). From Table V it can be seen that (taking averages) halite from Detroit and halite from Avery Island, Louisiana, differ in their chlorine isotope abundance ratio by $+0.012 - (-0.012) = 0.024$, or 24 parts in approximately 3100. The probability that this difference was caused by instrumental variation was calculated using the method given in Appendix II, and was found to be zero within the limits of the mathematical tables.

In order to check these data and also the reproducibility of the method, two other samples of dichlorotetrafluoroethane were prepared starting from halite samples from Avery Island and from Detroit, which were labelled simply as Samples A and B, respectively. Samples A and B were analysed by direct comparison, that is, with one of them serving as the "standard", on Mass Spectrometer No. 3. The results obtained (Table V) show that the halite from Detroit has an isotope abundance ratio greater than that of the halite from Avery Island by an average of $\frac{0.019 - (-0.012)}{2} = 0.016$, or 16 parts in approximately 3100. This result is in reasonably good agreement with the 24 parts in 3100

obtained with Mass Spectrometer No. 2, when each sample was analysed by comparison with a third sample as "standard".

(a). Synthetic Materials Containing Chlorine

Before discussing the exchange of chlorine isotopes between chlorate and chloride ions, a few remarks concerning dichlorotetrafluoroethane samples 10 and 11 are in order.

It was noticed in the mass spectrometric analyses of dichlorotetrafluoroethane prepared from potassium chlorate (Sample 3, Table VI) that the $\text{Cl}^{35}/\text{Cl}^{37}$ ratio was somewhat high relative to that of the "standard" by an average value of 16.5 parts in approximately 3100. As one might have expected an enrichment of Cl^{37} in a chlorate salt (11), two samples, one of sodium chloride and one of sodium chlorate prepared by electrolysis from the sodium chloride, were obtained and analysed as described.

The results of these analyses (Samples 10 and 11, Table VI) show that the sodium chlorate has a slightly higher (5 parts in approximately 3100) isotope abundance ratio than that of the sodium chloride.

It is suggested that, while, thermodynamically, Cl^{37} would be expected to concentrate in the chlorate, the electrolysis reaction converting $(\text{Cl}^{35})^-$ to $\text{Cl}^{35}\text{O}_3^-$ may be more rapid than the corresponding reaction involving Cl^{37} .

Turning to the exchange experiments, the data in Table VI show that the dichlorotetrafluoroethane Samples 3 and 5 both have

a higher isotope abundance ratio ($\text{Cl}^{35}/\text{Cl}^{37}$) than the "standard", but that Sample 5, on the average, has an isotope abundance ratio of 6 parts in 3100 less than that of Sample 3, corresponding to a slight enrichment of Cl^{37} in Sample 5, relative to Sample 3. As Sample 5 was prepared from the same chlorate as Sample 3 after nineteen days equilibration with potassium chloride of the same isotope abundance ratio, the difference of 6 parts in 3100 corresponds to a slight exchange of chlorine isotopes in the direction predicted by the theoretical equilibrium constant. (The small amount of potassium chloride recovered from Solution No. 1 along with the potassium chlorate should tend to make the 6 parts in 3100 a slightly low estimate of the difference in samples 3 and 5.)

The results shown in Table VI for dichlorotetrafluoroethane sample 7 are interesting, since this material, potassium chlorate, (from Solution No. 2) was allowed to equilibrate for a shorter time (16 days instead of 19) but shows a much larger difference from Sample 3 and Sample 5 does. The average difference in isotope abundance ratio between Samples 3 and 7 is 26 parts in 3100 (calculated from the data of Table VI).

It seems, therefore, that some exchange of the isotopes of chlorine can be obtained between chloride and chlorate ions in solution, especially in the presence of a small amount of sulfuric acid (the essential difference between the contents of Solutions No. 1 and No. 2 from which dichlorotetrafluoroethane Samples 5 and 7 were prepared, respectively).

CONCLUSIONS

The method of mass spectrometric analysing chlorine using dichlorotetrafluoroethane is a convenient and useful one. Purification of the tetrafluoroethylene formed by the thermal decomposition of "Teflon" is desirable, but once a supply of this compound has been prepared and stored the preparation of dichlorotetrafluoroethane by direct union of chlorine and tetrafluoroethylene can be accomplished rapidly and conveniently. This is in contrast to the preparation of carbon tetrachloride which is otherwise a useful substance for the mass spectrometric analysis of chlorine.

The performance of dichlorotetrafluoroethane in the mass spectrometer leaves little to be desired; it is apparently non-corrosive, and exhibits no "memory effects", in contrast with, say, arsenic trichloride, hydrogen chloride, or chlorine itself.

Seven naturally-occurring chlorides were investigated; six samples of halite and one of carnallite. Five of the chlorides come from different areas, and of these, four were intercompared by analyses involving the same "standard". Two comparisons were also made between pairs of samples from the same localities. With respect to the latter, the fact that no difference in the isotope abundance ratio of chlorine was found in halite taken from different depths in two different salt beds

indicates that little preferential solubility exists between the isotopic modifications of sodium chloride, or, that the salt beds were laid down under non-equilibrium conditions. The suggestion that a pair of samples may have come from equivalent "isotopic positions" within fractionated layers in a given bed seems unlikely in view of the similar results obtained with samples from two different beds.

Considering the four samples from different localities, the isotope abundance ratios for two were sufficiently similar to each other and to that of the "standard" as to give no grounds for considering that a natural variation existed. The isotope abundance ratios of the other two, however, were sufficiently different, both when compared with each other directly, and when compared indirectly through the "standard", that it is considered that a natural variation has been established. The differences found (between halite from Detroit, Michigan and halite from Avery Island, Louisiana) in the $\text{Cl}^{35}/\text{Cl}^{37}$ ratio were between 16 and 24 parts in approximately 3100, or about 0.5 to 0.8%. This corresponds to an average difference of 0.0024 units in the atomic weights. In this investigation only a relatively few samples were studied, and the differences found concern only two similar minerals. The actual variation in nature may be considerably larger; Urey has suggested "that a difference of 0.031 atomic weight units may exist", (11).

Experimental evidence has been obtained to indicate

that a slight fractionation takes place during the electrolytic preparation of sodium chlorate from sodium chloride.

While it appears that some separation of isotopes may be obtained through the exchange of chlorine between chlorate and chloride ions in solution, further work is necessary to establish this with certainty.

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APPENDIX I

STATISTICAL METHOD FOR THE COMPARISON OF AN "UNKNOWN" WITH ITS BRACKETTING STANDARDS

Nomenclature

Subscripts

A subscript preceeding a character is invariably associated with the "standard" and refers to the position of the particular "standard", either preceeding the unknown (1), or following (2).

Characters

x	individual isotope abundance ratio (I.A.R.) calculated from one spectrogram of a "standard".
y	same as (x) only with reference to an "unknown".
\bar{x}	mean I.A.R. from one "standard".
\bar{y}	mean I.A.R. from one "unknown".
\bar{X}	mean of $1\bar{x}$ and $2\bar{x}$
\bar{Y}	same as \bar{y}
$m_{\bar{x}}$	theoretical \bar{x}
$m_{\bar{y}}$	theoretical \bar{y}
σ	theoretical standard deviation ("unknown" and "standard")
$\hat{\sigma}_{\bar{x}}$	"unbiased estimate" of standard deviation of \bar{x}
$\hat{\sigma}_{\bar{y}}$	" " " " " " \bar{y}
n_x	no. of spectrograms contributing to \bar{x}
n_y	no. of spectrograms contributing to \bar{y}
$N_{\bar{x}}$	$1^{n_{\bar{x}}}$ plus $2^{n_{\bar{x}}}$
$N_{\bar{y}}$	same as n_y

Assumptions

- (1) that \bar{x} and \bar{y} are independently and normally distributed, or approximately so.
- (2) that σ is the same for both "standard" and "unknown".

Theory

The hypothesis is then set up that $m\bar{x} = m\bar{y}$ and the probability that this is so calculated. (A probability of less than 0.05 is considered a negative answer).

If the hypothesis is true then

$$\sigma_{\bar{x}-\bar{y}} = \sqrt{\frac{\sigma_x^2}{N_x} + \frac{\sigma_y^2}{N_y}}$$

and, therefore, t (t^2 is the power to which "e" is raised in a normal distribution function)

$$= \frac{\bar{x} - \bar{y}}{\sigma_{\bar{x}-\bar{y}}}$$

The probability that the difference between the "standard" and "unknown" I.A.R.s ($\bar{x} - \bar{y}$) confirms or rejects the hypothesis may then be obtained from a table containing the probability that various values of "t" will be exceeded.

APPENDIX II

STATISTICAL METHOD FOR THE COMPARISON OF ONE "UNKNOWN"
 IN THE SPECIAL CASE WHERE TWO ANALYSES OF EACH ARE
 AVAILABLE

Nomenclature

Subscripts

These are the same as for APPENDIX I, and also as follows: subscripts following a character refer to first, the experimental number assigned the "unknown" or in the case of a "standard" the "unknown" with which it is associated, and secondly the Analysis Number.

Characters

The same as those listed in APPENDIX I.

Assumptions

The same as those for APPENDIX I.

Theory

There are two analyses each of "unknown" (i) and "unknown" (j) (an analysis refers to a set of, "standard", "unknown" "standard") which are normally distributed thus:

$I \quad f(\bar{x}_{i1}) = N\left(m_{\bar{x}_{i1}}, \frac{\sigma^2}{n_{\bar{x}_{i1}}}\right)$ $f(\bar{y}_{i1}) = N\left(m_{\bar{y}_{i1}}, \frac{\sigma^2}{n_{\bar{y}_{i1}}}\right)$ $f({}_2\bar{x}_{i1}) = N\left(m_{\bar{x}_{i1}}, \frac{\sigma^2}{n_2\bar{x}_{i1}}\right)$	III	$f(\bar{x}_{j1}) = N\left(m_{\bar{x}_{j1}}, \frac{\sigma^2}{n_{\bar{x}_{j1}}}\right)$ $f(\bar{y}_{j1}) = N\left(m_{\bar{y}_{j1}}, \frac{\sigma^2}{n_{\bar{y}_{j1}}}\right)$ $f({}_2\bar{x}_{j1}) = N\left(m_{\bar{x}_{j1}}, \frac{\sigma^2}{n_2\bar{x}_{j1}}\right)$
$II \quad f({}_1\bar{x}_{i2}) = N\left(m_{\bar{x}_{i2}}, \frac{\sigma^2}{n_1\bar{x}_{i2}}\right)$ $f({}_2\bar{y}_{i2}) = N\left(m_{\bar{y}_{i2}}, \frac{\sigma^2}{n_2\bar{y}_{i2}}\right)$ $f({}_2\bar{x}_{i2}) = N\left(m_{\bar{x}_{i2}}, \frac{\sigma^2}{n_2\bar{x}_{i2}}\right)$	IV	$f({}_1\bar{x}_{j2}) = N\left(m_{\bar{x}_{j2}}, \frac{\sigma^2}{n_1\bar{x}_{j2}}\right)$ $f(\bar{y}_{j2}) = N\left(m_{\bar{y}_{j2}}, \frac{\sigma^2}{n_{\bar{y}_{j2}}}\right)$ $f({}_2\bar{x}_{j2}) = N\left(m_{\bar{x}_{j2}}, \frac{\sigma^2}{n_2\bar{x}_{j2}}\right)$

By combining and averaging the functions of \bar{x} in each set

(I, II, III, IV) we may write,

$$\begin{array}{ll}
 \text{I} & f(\bar{x}_{i1}) = N \left(M_x, \frac{\sigma^2}{N_{\bar{x}_{i1}}} \right) \\
 & f(\bar{y}_{i1}) = N \left(M_y, \frac{\sigma^2}{N_{\bar{y}_{i1}}} \right) \\
 \text{II} & f(\bar{x}_{i2}) = N \left(M_x + d_2, \frac{\sigma^2}{N_{\bar{x}_{i2}}} \right) \\
 & f(\bar{y}_{i2}) = N \left(M_y + d_2, \frac{\sigma^2}{N_{\bar{y}_{i2}}} \right) \\
 \text{III} & f(\bar{x}_{j1}) = N \left(M_x + d_1, \frac{\sigma^2}{N_{\bar{x}_{j1}}} \right) \\
 & f(\bar{y}_{j1}) = N \left(M_y + d_1, \frac{\sigma^2}{N_{\bar{y}_{j1}}} \right) \\
 \text{IV} & f(\bar{x}_{j2}) = N \left(M_x + d_1, \frac{\sigma^2}{N_{\bar{x}_{j2}}} \right) \\
 & f(\bar{y}_{j2}) = N \left(M_y + d_1, \frac{\sigma^2}{N_{\bar{y}_{j2}}} \right)
 \end{array}$$

making a change of variable of $m_{\bar{x}_{i1}}$ to M_x and

$m_{\bar{x}_{i2}}$ to $(M_x - d_2)$ etc., and a similar change for m_y .

Now as the subtraction of two normal distributions

leaves a normal distribution, we may write,

$$\begin{aligned}
 f(\bar{x}_{i1} - \bar{y}_{i1}) &= N \left\{ (M_x - M_y), \left(\frac{\sigma^2}{N_{\bar{x}_{i1}}} + \frac{\sigma^2}{N_{\bar{y}_{i1}}} \right) \right\} \\
 f(\bar{x}_{i2} - \bar{y}_{i2}) &= N \left\{ (M_x - M_y), \left(\frac{\sigma^2}{N_{\bar{x}_{i2}}} + \frac{\sigma^2}{N_{\bar{y}_{i2}}} \right) \right\} \\
 f(\bar{x}_{j1} - \bar{y}_{j1}) &= N \left\{ (M_x - M_y), \left(\frac{\sigma^2}{N_{\bar{x}_{j1}}} + \frac{\sigma^2}{N_{\bar{y}_{j1}}} \right) \right\} \\
 f(\bar{x}_{j2} - \bar{y}_{j2}) &= N \left\{ (M_x - M_y), \left(\frac{\sigma^2}{N_{\bar{x}_{j2}}} + \frac{\sigma^2}{N_{\bar{y}_{j2}}} \right) \right\}
 \end{aligned}$$

Combining the preceding four equations in pairs and

dividing by two gives,

$$f\left(\frac{\bar{x}_{i1} - \bar{y}_{i1} + \bar{x}_{i2} - \bar{y}_{i2}}{2}\right) = N \left\{ (M_x - M_y), \frac{\sigma^2}{4} \left(\frac{1}{N_{\bar{x}_{i1}}} + \frac{1}{N_{\bar{y}_{i1}}} + \frac{1}{N_{\bar{x}_{i2}}} + \frac{1}{N_{\bar{y}_{i2}}} \right) \right\}$$

$$f\left(\frac{\bar{x}_{j1} - \bar{y}_{j1} + \bar{x}_{j2} - \bar{y}_{j2}}{2}\right) = N \left\{ (M_x - M_y), \frac{\sigma^2}{4} \left(\frac{1}{N_{\bar{x}_{j1}}} + \frac{1}{N_{\bar{y}_{j1}}} + \frac{1}{N_{\bar{x}_{j2}}} + \frac{1}{N_{\bar{y}_{j2}}} \right) \right\}$$

Subtracting the last two functions yields a function

$$f \left\{ \left(\frac{\bar{X} - \bar{Y} + \bar{X} - \bar{Y}}{2} \right) - \left(\frac{\bar{X} - \bar{Y} + \bar{X} - \bar{Y}}{2} \right) \right\} \quad (A)$$

whose mean $(M_{yj} - M_{yi})$ has a standard deviation

$$\sigma_{j-i}^2 = \frac{\sigma^2}{4} \left\{ \frac{1}{N_{\bar{x}_{i1}}} + \frac{1}{N_{\bar{y}_{i1}}} + \frac{1}{N_{\bar{x}_{i2}}} + \frac{1}{N_{\bar{y}_{i2}}} + \frac{1}{N_{\bar{x}_{j1}}} + \frac{1}{N_{\bar{y}_{j1}}} + \frac{1}{N_{\bar{x}_{j2}}} + \frac{1}{N_{\bar{y}_{j2}}} \right\}$$

As an "unbiased estimate" of the standard deviation (σ)

we may take

D^2 = square of deviation of an I.A.R. from mean

$\sum D^2$ = sum of D^2 for one analysis

$$\hat{\sigma}_{j-i}^2 = \frac{\sum \sum D^2}{N_{\bar{x}_{i1}} + N_{\bar{y}_{i1}} + N_{\bar{x}_{i2}} + N_{\bar{y}_{i2}} + N_{\bar{x}_{j1}} + N_{\bar{y}_{j1}} + N_{\bar{x}_{j2}} + N_{\bar{y}_{j2}} - 12}$$

Now, using this last expression, and the difference between the means of the two "unknowns" given by (A) the probability that the difference is significant may be determined as in APPENDIX I, after calculation of