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A MASS SPECTROMETRIC ANALYSIS OF DC 704 DIFFUSION-PUMP OIL FRAGMENTATION

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ABSTRACT

This report presents a mass spectrometric analysis of DC 704 diffusion-pump fluid. An attempt is made to assign a structural formula for each major task. A table listing empirical formulae for each mass number is presented as well as the fragment source from which it is derived. A unique vapor source and inlet system is described.

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INTRODUCTION

The number of small mass spectrometer residual gas analyzers of limited range and mounted directly on a vacuum system is increasing steadily. Qualitative and quantitative analysis of the residual gas frequently leaves the novice with a confusing picture. In oil-pumped systems the small amount of backstreaming oil contributes peaks at nearly every mass number between 12 and 110. With such profusion of peaks the interpretation of the mass spectrometric record when molecular species from an unknown are present is frequently a best-guess effort. A chemical structure assigned to a peak can provide a clue to the composition of the unknown. This paper attempts to assign qualitative structural formulae for the peaks due to DC 704 diffusion-pump oil.

In order to obtain a clean record of the oil spectrum, uncontaminated with vapor from backing pumps, "O" ring outgassing, air leakage or solvents, the spectra presented were taken from an ion-pumped chamber into which DC 704 vapor was admitted. No qualitative difference was found between this spectrum and that obtained from an oil diffusion-pumped system, except that the starting background was cleaner.

APPARATUS

The mass spectrometer used in this study is a CEC 21-613. This is a small cycloidal type generically known as a residual gas analyzer. Its mass range from 1-150 is adequate for this study. With the spectrometer operated at 50 microamperes ionizing current, most peak shapes are unique and readable beyond m/e 120. Accelerating voltage is continuously varied automatically and constitutes the scan mechanism. Recorder chart speeds of 2 inches per minute provide good peak separation and peak shape.

Introduction of DC 704 vapor was accomplished by using a Knudsen cell as a reservoir, heated by two 50 watt resistors mounted along the long axis of the cell. Vapor was conducted from the cell orifice through heated copper tubing, through a shut-off valve and into the heated chamber of an ion pump (Figure 1).

Base pressure in the system before opening the shut-off valve was about 2×10^{-8} torr and since the Knudsen cell was differentially pumped, the system only lost a decade of pressure when the entire system was open.

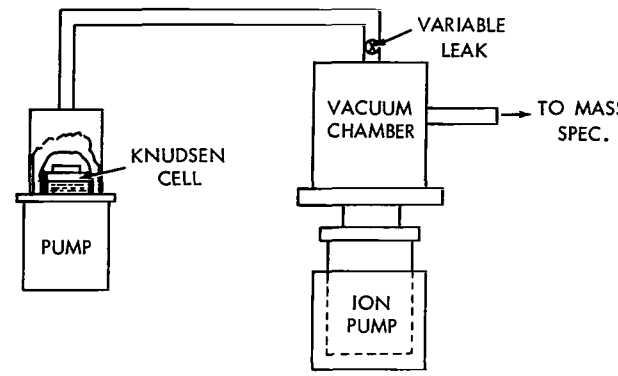
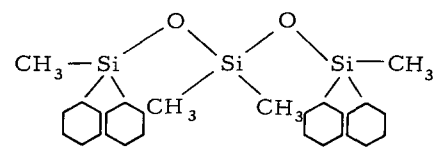


Figure 1 - Pumping cell showing the relationship of the Knudsen cell to the spectrometer.

CHEMISTRY

DC 704 diffusion-pump oil is a unique molecular specie, tetramethyltetraphenyltrisiloxane, with a molecular weight of 484.



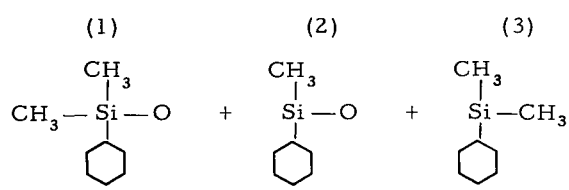
In the electron beam in the ionizing chamber of the spectrometer, enough energy is assumed to be present to fragment the molecular bonds. Dissociative bond energies in the siloxane molecule (Table 1) are approximate.

Table 1

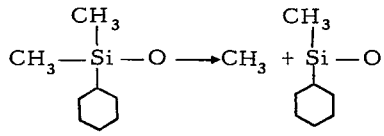
Dissociative Bond Energies in the Siloxane Molecule.

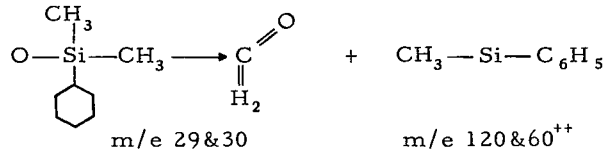
Bond	KCal
C-Si	78
Si-O	106
Si-C(H_3)	72
Si-C(C_5H_5)	87

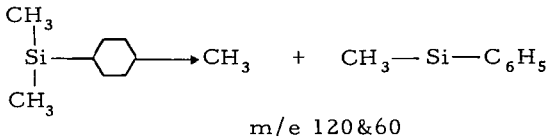
It must be remembered that many active ions and free radicals are present together after molecular fragmentation. Recombinations taking place under these circumstances give rise to ions which are very difficult to explain in classical chemical terms. Thus, from Table 1, the first probable rupture takes place between Si-CH_3, closely followed by Si-C. Recombination will produce toluene and xylene. Three major fragments are hypothecated:

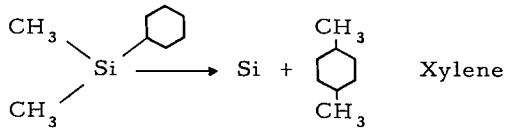


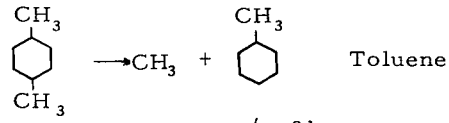
Peaks are found at these respective masses. The following reactions are suggested and peaks are found at each of the product masses:

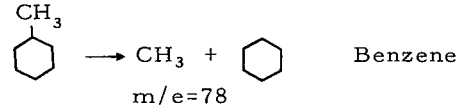
1.  which is identical to (2) above. m/e=136

2. 
m/e 29&30 m/e 120&60^{++}

3.  which is identical to equation 2.
m/e 120&60

4.  Xylene
m/e=106

5.  Toluene
m/e=91

6.  Benzene
m/e=78

Thus we arrive at three semi-major products which are well-known in the literature: xylene, toluene and benzene.* Table 2 summarizes the patterns; asterisks indicate peaks found and serve to emphasize uniqueness or congruency where there is an overlap.

Figure 2 is a mass spectrograph of the residual gas background of the cleaned but unbaked chamber. The chamber had been vapor degreased in trichlorethylene and despite subsequent polishing, m/e at 130, 97 and 95, parent and major peaks, indicate that absorbed solvent still remains. Figure 3 is the residual background of the chamber after baking at 200°C for 8 hours. The dominant peaks are the usual H_2O,N_2, and CO, not shown in the mass range selected.

*American Petroleum Inst. Research Project 44–Carnegie Inst. of Technology.

Table 2

DC 704 Fragmentation Patterns.

Mass	Ion	Xylene	Toluene	Benzene	Trichlorethylene
107	C_8H_{11}	*			
106	C_8H_{10}	*			
105	C_8H_9	*			
103	C_8H_7	*			
97	$C_2H_3Cl_2$				*
95	$C_2H\,Cl_2$				*
92	C_7H_8	*	*		
91	C_7H_7(Toluene)	*	*		
82	C_6H_{10}			*	
79	C_6H_7	*			
78	C_6H_6(Benzene)	*		*	
77	C_6H_5	*		*	
65	C_5H_5	*	*		
63	C_5H_3	*	*		
62	C_2H_3Cl				*
61	C_2H_2Cl				*
60	$C_2H\,Cl$				*
59	$C_2\,Cl$				*
52	C_4H_4(Alkynes)			*	
51	C_4H_3	*		*	
50	C_4H_2			*	
49	Ch_2Cl				*
48	$CH\,Cl$				*
47	$C\,Cl$				*
43	C_2H_{30}/C_3H_7				*
39	C_3H_3(Dienes)	*	*	*	
38	C_3H_2				*
36	$H\,Cl$				*
35	Cl				*
28	$CO + N$				
27	C_2H_3	*			
25	C_2H				*
24	C_2				*
15	CH_3	*	*	*	

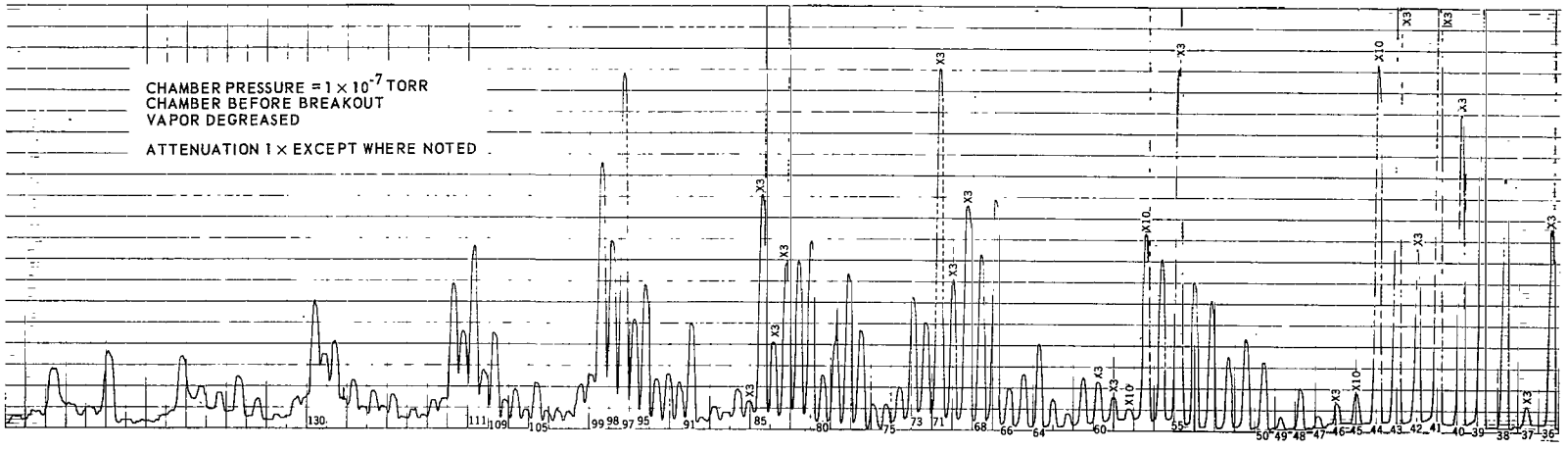


Figure 2—Mass spectograph of the residual background of unbaked chamber.

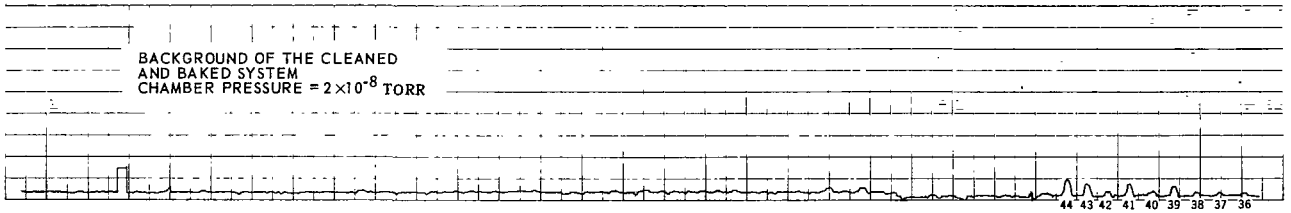


Figure 3—Residual background of mass spectrometer chamber after bakeout.

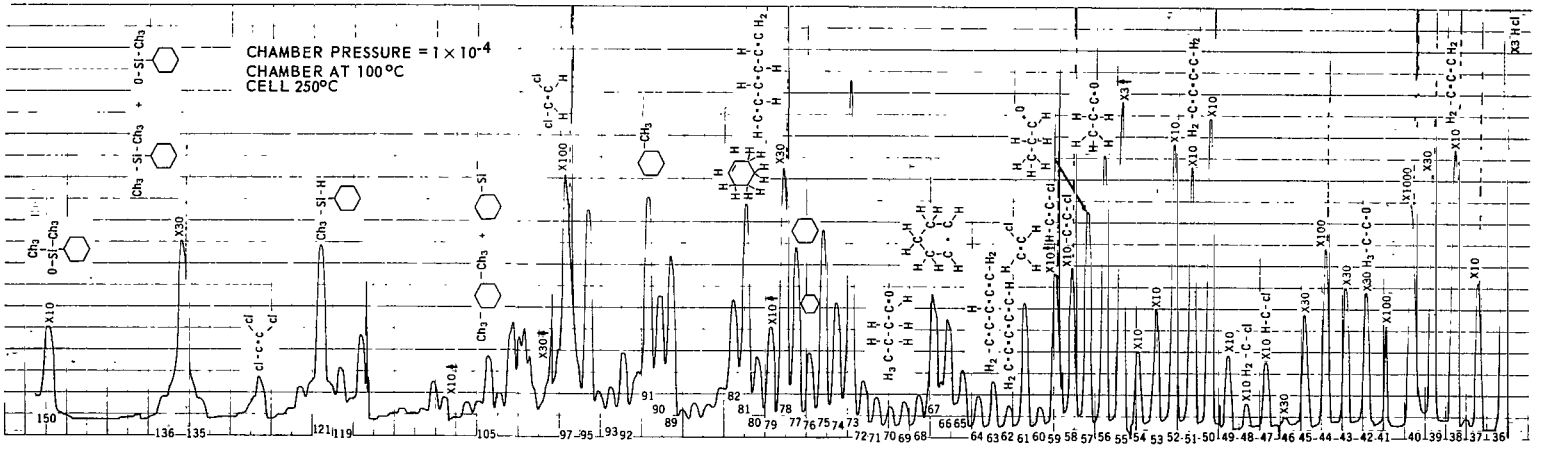
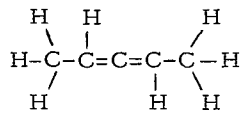


Figure 4—Fragmentation pattern of the diffusion-pump oil vapor.

Figure 4 is a spectrogram of the diffusion-pump oil vapor. Above each major peak is the chemical picture of the ion or molecule proposed for the corresponding mass number. Adjacent peaks are the result of the same ion usually with the loss of one H ion, or one mass number. Alternate structural formulae are completely possible, i.e., at mass 68 a 5 carbon ring is proposed for the general C_5H_8 molecule. A linear diene is equally possible:



Only a "best guess" is tendered based on the empirical formula assigned to the mass number.

CONCLUSIONS

The spectroscopist looking for oil contamination in a vacuum system using DC 704 as a pumping fluid must be able to resolve peaks beyond mass 107. Fragments of the oil molecule leave a record at masses 150 and 135 which eventually break down to the three well known patterns for xylene, toluene and benzene. These three appear in many organic materials such as the elastomers, as well as in cleaning materials commonly used in cleaning mass spectrometers; hence the need to examine the spectrum beyond mass 107.

A tentative conclusion reached by the authors is that it is extremely difficult, at least, to prevent some backstreaming of oil into the chamber. The oil-pumped vacuum system used in some of these experiments has the diffusion pumps doubly baffled. One baffle just above the pump throat circulates water, the next one is an optically tight, chevron liquid nitrogen-cooled type. At no time was the spectrum of oil absent despite constant cleaning with toluene followed by ether. The ion pump, however, after baking, gave a clean base line. This reaffirms what has appeared time and again in the literature—that baking is required to furnish a completely clean vacuum chamber when no fresh vapor is constantly being added.

(Manuscript received June 3, 1965)

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