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MASS SPECTROMETER STUDIES OF HIGH VACUUM MATERIALS

By

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John R. Sites
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ABSTRACT

Observations were made of the most abundant ions in a mass spectrometer upon heating materials commonly used in high vacuum work. Materials investigated were teflon, silicon rubber and octoil-S diffusion pump oil.

MASS SPECTROMETER STUDIES OF HIGH VACUUM MATERIALS*

John R Sites and Russell Baldock

In many cases it is desirable to raise the temperature of a complete vacuum system to aid in the outgassing of unwanted vapors. With the use of metal systems, and especially systems which have flanges which are often opened for adjustments or replacements, the outgassing characteristics of gasket materials are of interest. Soft metal gaskets are frequently used, but for some applications a more resilient gasket may be desired. Some examples of the latter type are ordinary rubbers, synthetic rubbers, silicone or silastic rubbers, and some plastics not included above.

As reported by C. E. Normand and W. R. Rathkamp,[1] some of the easily available and seemingly desirable materials have relatively poor outgassing qualities, even at room temperatures Two of the materials tested by them, silicone rubber and teflon, were chosen for study in the mass spectrometer to find what contributed to the outgassing at room temperature, and at temperatures at which vacuum systems are usually outgassed. A sample of octoil-S diffusion pump oil was also investigated.

The apparatus used was a 60 degree Nier type all metal mass spectrometer[2] with a source oven for distilling vapors from solid samples into the ionization chamber. The accelerating potential was 2000 volts, and the ionizing electron energy was 75 volts.

Silicone rubbers are made of dimethylsiloxane which have been polymerized and cured in some specified manner. Fillers, catalytic curing agents, and other proprietary ingredients are added. The sample investigated by us was a 3/8-inch length of 1/16-inch diameter O-ring material. It was placed in the sample container of the mass spectrometer source oven and mass scans were taken at various temperatures.

Figure 1 shows the mass cracking pattern obtained at a temperature of 195°C. The notation is simplified by identifying each bar on the graph by

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* Presented at the Southeastern Section of the American Physical Society at North Carolina State College, Raleigh, N.C., April 10, 11 and 12, 1952.

1. Norman, C. R. and W. R. Rathkamp, "Evaluation of Vacuum Gasket Materials" Southeastern Section of American Physical Society, April 5-7, 1951.
2. Baldock, Russell and John R. Sites, "A Versatile All-Metal 60° Mass Spectrometer", Document No. Y-755.

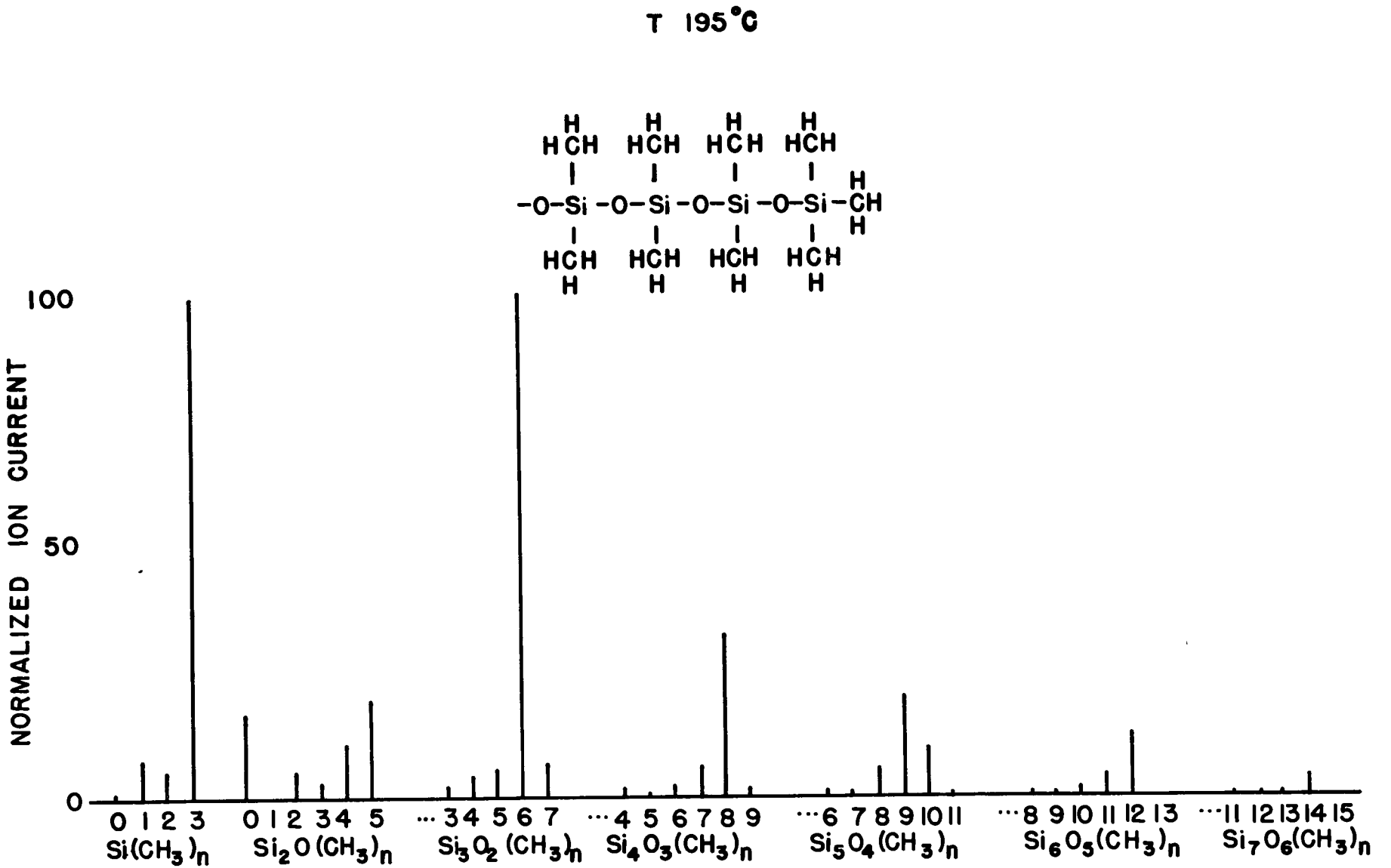

FIGURE 1. MASS CRACKING PATTERN OF SILICONE RUBBER

the number of methyl radicals associated with the indicated number of silicon and oxygen atoms. Also shown is the general formula of the silicone polymer.

The series of ions presented is from the fragments formed by various groupings of dimethylsiloxanes which have lost one or more methyl groups and have a hydrogen recombining in their places. Each main group is 74 mass units above the previous one, just the mass of one dimethylsiloxane group. Not indicated are the minor ions formed by the stripping of one or more hydrogen atoms from some of the methyl groups, and an unidentified series of single ions with the lowest member at mass 81. It is interesting to note that there was no indication of the breaking of the silicon-oxygen bond in the siloxane grouping by the 75 volt electrons. At the lower temperatures in the first part of the tests, ions from hydrocarbons, possibly oils, appeared in great abundance and intensity. These diminished greatly as the temperature was raised, and they were pumped out. The intensity of the lower mass silicone ions increased with increase in temperature, while the higher mass ions decreased.

Figure 2 shows the mass cracking pattern obtained from a piece of sheet teflon cut to the same dimensions as the previous silicone rubber sample. No ions different from background were found until the sample had been heated to about 250°C, when the indicated ions started to appear. The data that are presented were taken at 361°C, about 150°C higher than the temperature for the silicone sample.

In the section on the thermal stability of fluorocarbons found in the book, entitled, Fluorine Chemistry and edited by J. H. Simons, T. J. Brice discusses teflon, or chemically polytetrafluoroethylene. He states that decomposition by heat at low pressures gives carbon tetrafluoride (CF_4), tetrafluoroethylene (C_2F_4), hexafluoropropylene (C_3F_6), and cyclofluorobutane (C_4F_8). The data presented here confirm this, with the ions of the parent molecule with one fluorine atom removed predominating, and the ions of the parent nearly as strong. No ions were found which could not be accounted for, in fact, quite a number of ions that might be expected were not present. The patterns in each group of the series are very different from those found for the lower straight chain fluorocarbons as reported by Mohler in 1949 in the Journal of the American Chemical Society.

Figure 3 shows the mass cracking pattern obtained when one drop of octoil-S was maintained in the ion source oven, at 155°C. This widely used diffusion pump oil is di-2-ethyl hexyl sebacate, the formula is included in Figure 3. The main groupings in the series differ by 14 mass units, indicating the addition of a CH_2 radical to the group next lower in the series. Note the change in characteristic group pattern after the C_4 group, as one might predict from the branching in the structural formula. Note also the small relative abundance of the C_7 group. Only a few small unidentified ions appeared above mass 112.

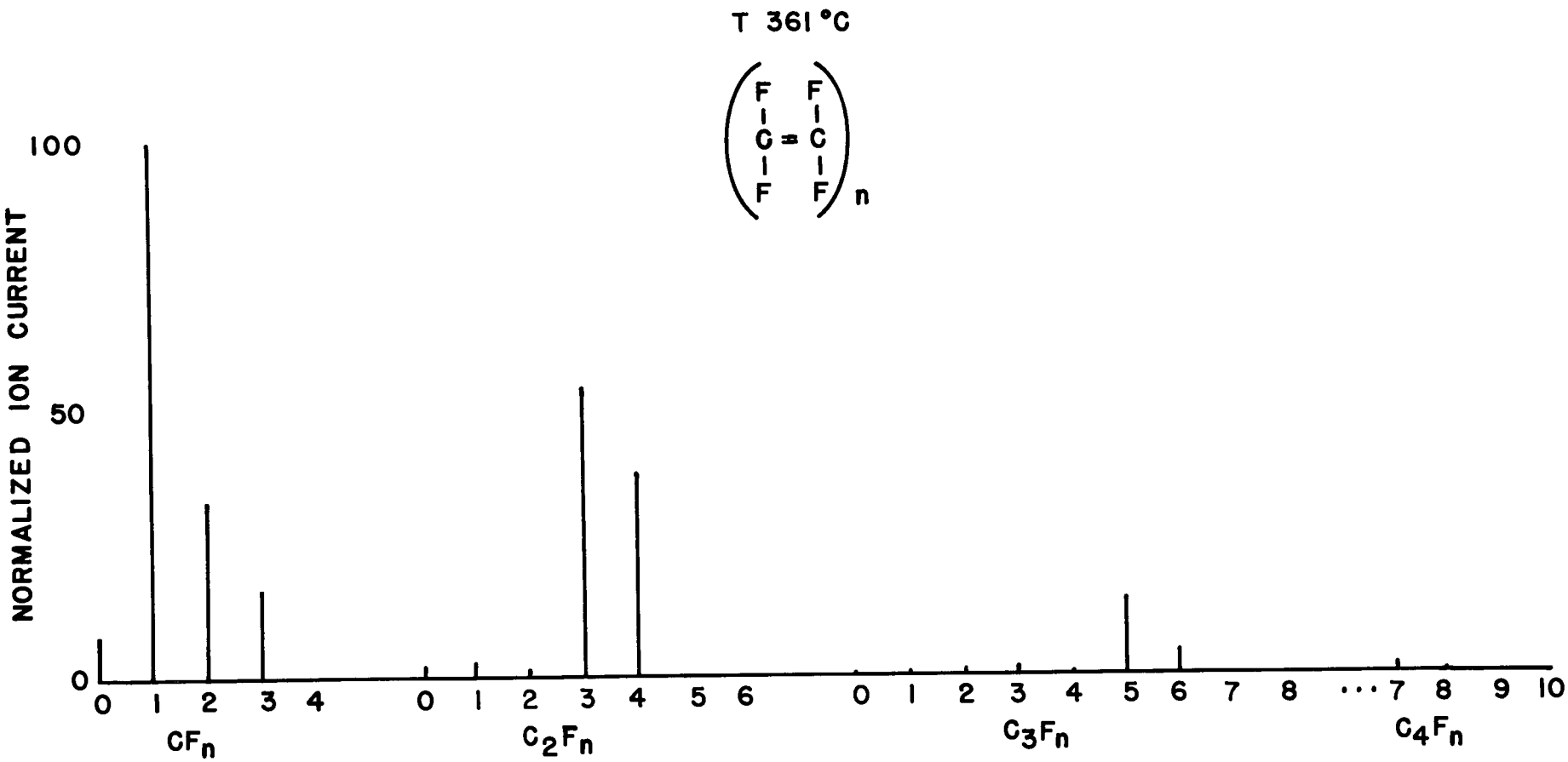

FIGURE 2. MASS CRACKING PATTERN OF TEFLON

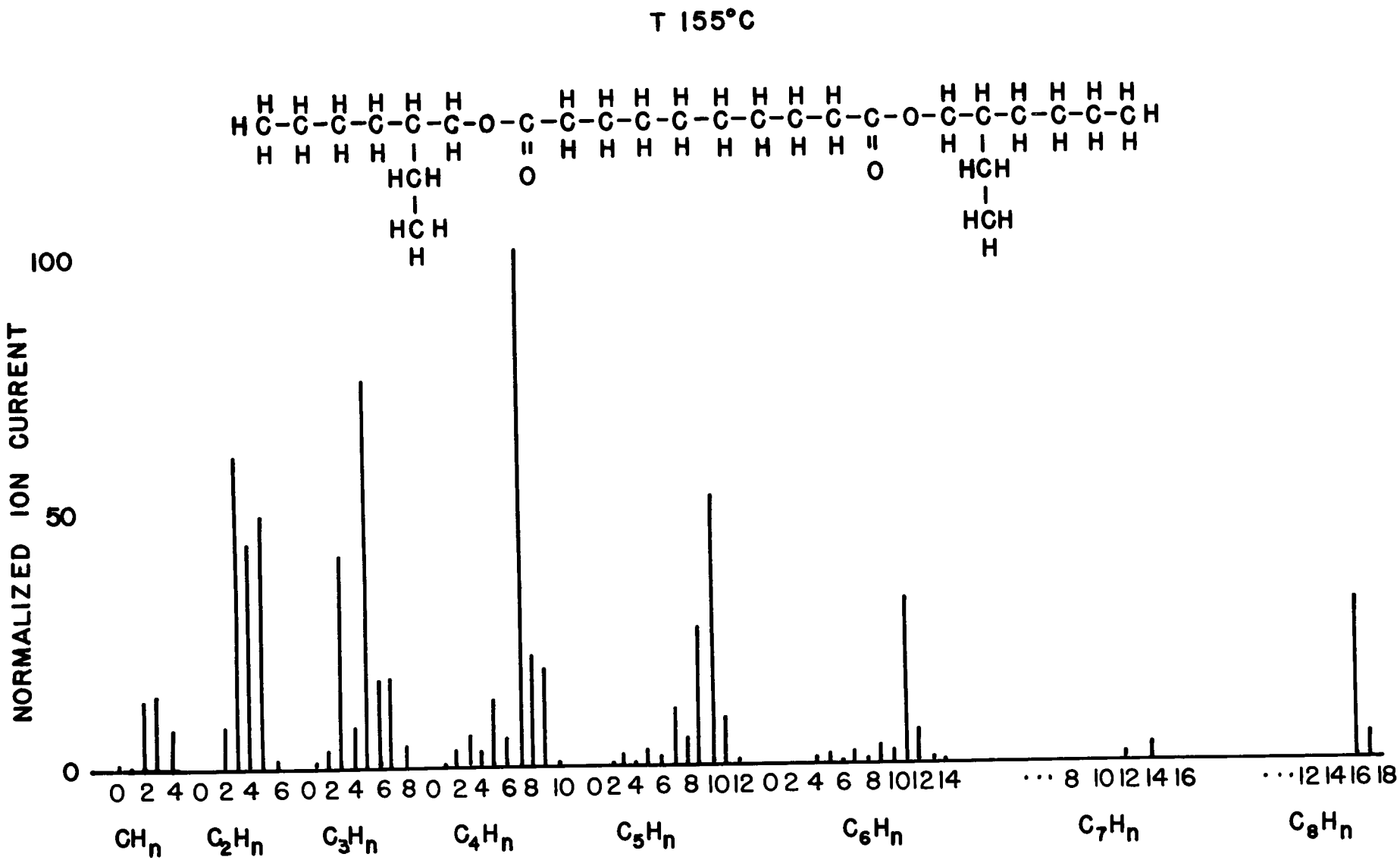

FIGURE 3. MASS CRACKING PATTERN OF OCTOIL-S

The distribution of ions obtained in the mass spectrometer by purposely introducing octoil-S is in great contrast to the distribution resulting, say, after a cold trap which is ahead of a diffusion pump using octoil-S has been allowed to run dry. Upon one extreme occasion we recorded ions at essentially every mass unit up to at least mass 350, in characteristic groups spaced at 14 mass units apart. These probably were ions of volatile products of cracking or oxidation of the hot oil.

Figure 4 is a photograph of the gasket samples before and after being heated in the mass spectrometer. The teflon was cut from a sheet which apparently is anisotropic, and it expanded as shown. A gasket made of sheet material under compression would have no chance to alter its shape in this manner. The silicone rubber sample became very brittle after being heated to 250°C, changing to a powder when crushed mildly. It had lost its resilience and usefulness as a possible gasket material.

From the comparisons presented for this sample of silicone rubber and teflon, one may conclude that teflon is better because it must be heated to a higher temperature before appreciable outgassing or vaporizing takes place, and because it has fewer, simpler ion fragments. Also, this sample of silicon rubber apparently had hydrocarbons associated with it, even after being cleaned in chloroform before it was placed in the mass spectrometer. The physical properties of the silicone were also poor after being heated to about 250°C.

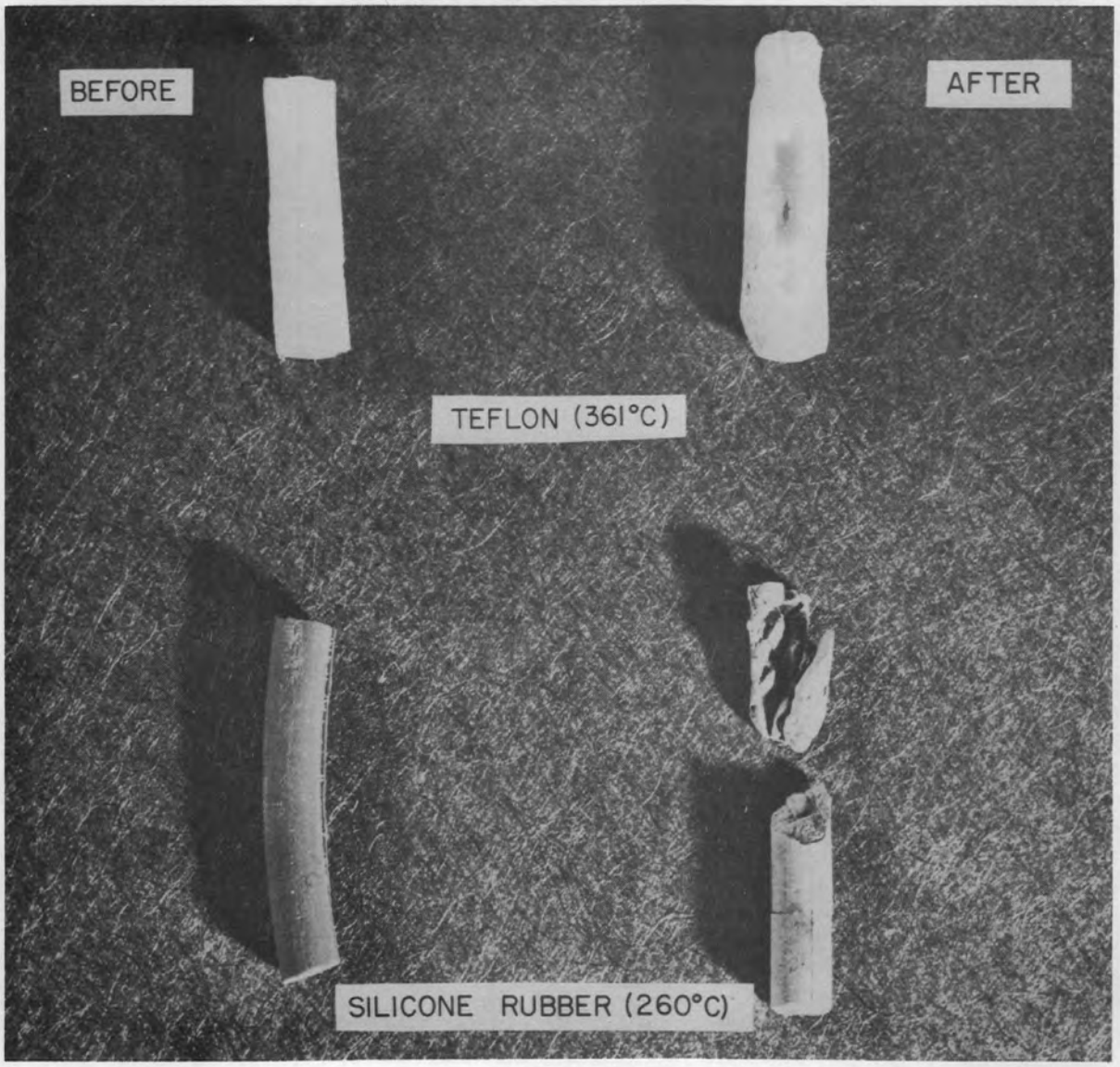

FIGURE 4. MASS SPECTROMETER SAMPLES