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# MECHANISM OF FORMATION OF CERTAIN METASTABLE PEAKS NOTED ON A CYCLOIDAL FOCUSING MASS SPECTROMETER*

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## SUMMARY

A previous investigation allowed extended contact between the heated stainless-steel cycloid envelope of the mass spectrometer and gaseous mixtures consisting primarily of hydrogen chloride and water. Because of this contact, roughening of the stainless-steel walls occurred. Backgrounds run with helium showed prominent peaks of definite metastable shape. Similar peaks appeared during procedures for carbiding the tungsten filament. At least eight different metastable peaks were recorded, ranging in mass number from 20 to 260. The metastable peaks are postulated to result from decompositions of iron, chromium, and nickel carbonyls.

Author

## INTRODUCTION

Mass spectroscopy has been invaluable in the analysis of anionic impurities in the surface region of ionic solids such as sodium chloride. Two methods of analysis have been perfected and are in use at Lewis Research Center (refs. 1 and 2). Analyses using these methods resulted in repeated exposure of the stainless-steel cycloid envelope of the mass spectrometer to gaseous mixtures consisting largely of water ($H_2O$) or $H_2O$ and hydrogen chloride (HCl). Despite the reactive nature of these mixtures, surprisingly little difficulty was encountered through many hundreds of analyses[1]. However, out-of-the ordinary behavior, when eventually encountered, consisted of the presence in the spectra of prominent metastable peaks, pressure bursts during filament carbiding, and loss of sensitivity. It is the intent of the present report to summarize the problems encountered, to provide an explanation of their cause, and to present procedures for eliminating them. The explanation presented is consistent not only with the anomalous behavior observed but is also supported by certain planned experiments designed to clarify specific aspects of these problems.

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[1] On one occasion, a sample containing hydrogen chloride had to be left in the analysis chamber for 16 hours because of power failure to the instrument. The only trouble encountered at that time was a longer pump-down time than normal.

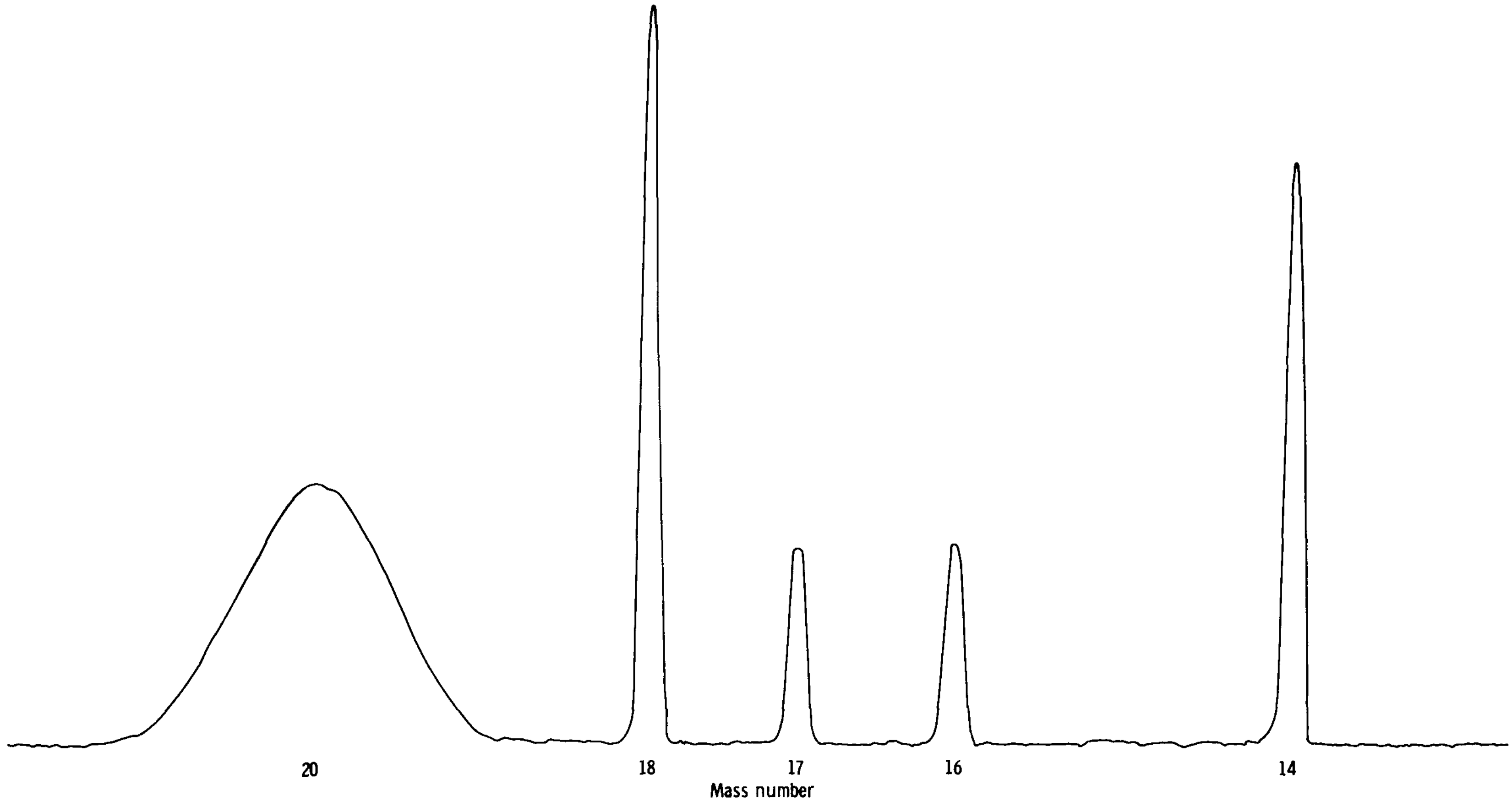

Figure 1. - Portion of spectrum showing metastable peak.

These observations and experiments are described in the following sections.

## OBSERVATIONS

Observance of not only an excessive but also a variable background for mass numbers 44, 28, and 32 was the first clear indication of a problem. Since the analyses required determining carbon dioxide ($CO_2$) in the nanomole range, this was an intolerable situation. (The $CO_2$ background at that time was approximately 30 to 40 nanomoles.) The usual procedure of baking out the charcoal trap of the 21-620 mass spectrometer did not alleviate this problem. The inlet system and the cycloid envelope were thoroughly cleaned and the filament replaced but not carbided. The first backgrounds run were again at normal levels. However, backgrounds run with helium (He) showed the presence of a number of additional prominent, broad peaks that had the appearance of metastables. A portion of one such spectrum is shown in figure 1. The peak occurring approximately at mass number 20 is far different in shape from the normal peaks at mass numbers 14, 16, 17, and 18. The extra peaks at higher mass numbers were, in general, considerably broader than the one shown in figure 1.

Further difficulties were encountered during attempts to carbide the new tungsten filament of the mass spectrometer. The normal procedure consists of maintaining a suitable pressure of butene in the analysis chamber for 2 to 4 hours and then butane for 2 hours. This is accomplished by keeping the pressure in the inlet system between 400 and 600 microns and allowing the gas to molecularly diffuse into the analysis chamber. Carbiding progressed normally for the first hour, with a pressure of approximately 0.03 micron present in the analysis chamber. Then sudden pressure bursts began to occur. Momentary pressure values of 0.2 to 0.3 micron were noted on the cold cathode gage. Such pressures are sufficiently large to activate the filament protection circuit. In order to keep the filament on so that carbiding could proceed, the pressure had to be reduced to approximately 1/4 its usual value. During carbiding, with either gas present, prominent peaks were noted that also had the appearance of metastables. Neither of these problems had been observed before during the carbiding process.

Moreover, the instrument then showed reduced sensitivities to gases such as nitrogen ($N_2$) and $CO_2$. Typical values are shown in table I. Sensitivities did not change markedly during the period when metastables were being observed. As can be seen in table I, the least reduction in sensitivity was observed for argon and the greatest for $H_2O$, but there is no obvious correlation with molecular weight. The reduced

TABLE I. - INSTRUMENT SENSITIVITIES PRIOR TO AND DURING PRESENCE OF METASTABLES.

| Gas | Typical sensitivity in absence of metastable, divisions per micron | Typical sensitivity in presence of metastable, divisions per micron | Sensitivity ratio |
|---|---|---|---|
| Water | 89 | 25 | 3.6 |
| Carbon monoxide | 120 | 48 | 2.5 |
| Nitrogen | 116 | 45 | 2.6 |
| Oxygen | 88 | 36 | 2.4 |
| Argon | 120 | 59 | 2.0 |
| Carbon dioxide | 108 | 37 | 2.9 |

sensitivities prevented detection of nanomole quantities of $CO_2$ from carbonate impurities. Since there had been no change in the leak rate of $CO_2$, the reduced sensitivity was not due to less gas in the analysis chamber itself.

## EXPERIMENTS AND EVALUATIONS

In order to determine the origin of the additional peaks, gas samples were introduced in various sequences and the presence or absence of metastable peaks was noted. It soon became obvious that the effect was not due to impurities in the He. After prolonged monitoring of a sample of He, metastable peaks would eventually disappear. If a new sample were then introduced, the metastables did not reappear. Evidently the He was acting to elute something from the instrument walls. Metastables were noted when He, butane, or butene immediately followed an introduction of carbon monoxide (CO) into the instrument and occasionally when He, butene, or butane was introduced following a period of several days during which the mass spectrometer was maintained in standby condition. Presumably under the latter conditions, the residual CO in the vacuum system became large enough to produce the effect.

There were two types of metastable spectra, one found when He was used as an elutant and another when hydrocarbons were used. In the case of the hydrocarbon elution, it is assumed that the adsorbed species leading to metastable peaks were more completely replaced because of the greater intensities for the common peaks and the greater variety of smaller peaks noted.

It was also observed that metastable peaks could be eliminated or reduced by alternately sampling CO and He for an hour each. The procedure was repeated until eventually no metastables were produced under any of the above conditions. An interpretation of this will be presented in the following section. Following filament replacement, normal sensitivities were again obtained for the various gases. Therefore, it must be concluded that the instrument's ability to perform satisfactory gas analysis was restored by the alternate-sampling treatment.

Inspection of the analysis chamber, however, revealed a pronounced roughening of the cycloid envelope. The roughening may have resulted from oxidation of the envelope by water vapor. Gulbransen and coworkers have observed that localized crystal growths, both whisker and platelet, are formed when pure iron is oxidized either in pure water vapor or in pure oxygen (ref. 3). Gulbransen also observed platelets of chromic oxide ($Cr_2O_3$) in the oxidation of stressed stainless steel in an atmosphere of wet oxygen containing trace amounts of hydrogen chloride (ref. 4). It is likely that these rough areas would provide the so-called "active sites" where reactions could occur that might generate the species causing the metastable peaks. The eventual inability to produce metastables could be interpreted to mean that active sites were no longer available.

## INTERPRETATION

Three potential reactions that can yield poorly focused peaks of what is called metastable shape are charge-exchange reactions yielding metastables, ion-molecule reactions, and free radical exchange reactions (ref. 5, pp. 251 to 262, 275 to 282, and 437 to 440, respectively). Careful scrutiny of the data leads one to prefer the first of these because of applicable chemistry and the calculations to be described below. No pressure dependence was found. On this basis, ion-molecule reactions are unlikely. Also, since the source pressure was low, it is unlikely that poorly focused peaks would have resulted from free radical reactions.

Reactions consistant with the experiments were considered which could produce metastables at masses where they were observed experimentally. These calculations were made using the general equation (ref. 5, p. 252)

$$m^* = \frac{m_2^2}{m_1} \tag{1}$$

where

$m^*$ apparent mass recorded

$m_1$ mass of original ion

$m_2$ mass of final ion resulting from transition

$$m_1^+ \rightarrow m_2^+ + (m_1 - m_2)$$

Metastables were observed at eight different mass numbers at various times; of these, the ones most often encountered centered at approximate mass numbers 20, 90, and 177. These three were generally the only ones observed when He was used for elution.

All the reactants and the reaction conditions were present which are known to lead to the formation of transition metal carbonyls. In the particular instrument used, heaters maintain a source temperature of approximately 250° C; the cycloid envelope itself, while not that hot, is sufficiently warm to permit carbonyl formation. Therefore, the assignment of the metastables using possible transition metal carbonyls was considered (especially those of iron (Fe), nickel (Ni), and chromium (Cr), the principal elements present in stainless steels). Since the stainless-steel envelope had been attacked by moist HCl, it is quite plausible that metal chlorides and metal oxychlorides were formed on its surface. Possible peaks arising from these compounds and carbonyls of these metals are compared in table II with the observed peaks.

The decomposition reactions presented in table II are reasonable ones because mass spectrometric studies conducted by Winters and Kiser on several transition metal carbonyls indicated that CO groups are indeed readily lost in the breakdown of ions of the type $M(CO)_x^+$ (refs. 6 and 7). (Since they used a time-of-flight mass spectrometer, metastables could not be observed.) Some of the expected peaks (e.g., $M^+$) were not detected in the spectra. Nevertheless, the chemical evidence is strongly in favor of carbonyl formation.

## TABLE II. - TENTATIVE IDENTIFICATION OF METASTABLES OBSERVED

| Eluting agent | Approximate mass numbers | | Decomposition reaction leading to metastable in mass spectrometer |
|---|---|---|---|
| | Observed | Calculated (a) | |
| Helium | 20 | 20 | $\mathrm{Ni(CO)_4^+ \rightarrow Ni^+ + 4\ CO}$ |
| | | 20 | $\mathrm{Cr(CO)_3^+ \rightarrow Cr^+ + 3\ CO}$ |
| Butene or butane | 64 to 66 | 64 | $\mathrm{Fe(CO)_5^+ \rightarrow Fe(CO)_2^+ + 3\ CO}$ |
| | | 65 | $\mathrm{Ni(CO)_2^+ \rightarrow Ni(CO)^+ + CO}$ |
| Butane | 72 | 71 | $\mathrm{Cr(CO)_4^+ \rightarrow Cr(CO)_2^+ + 2\ CO}$ |
| | | 75 | $\mathrm{Fe(CO)_4^+ \rightarrow Fe(CO)_2^+ + 2\ CO}$ |
| Butene | 82 to 85 | 84 | $\mathrm{CrCl_2(CO)_2^+ \rightarrow CrCl_2^+ + 2\ CO}$ |
| | | 86 | $\mathrm{Cr(CO)_3^+ \rightarrow Cr(CO)_2^+ + CO}$ |
| Helium or butane | 90 | 90 | $\mathrm{Fe(CO)_3^+ \rightarrow Fe(CO)_2^+ + CO}$ |
| | | 91 | $\mathrm{Ni(CO)_3^+ \rightarrow Ni(CO)_2^+ + CO}$ |
| Helium | 100 | 98 | $\mathrm{NiCl(CO)_2^+ \rightarrow NiCl(CO)^+ + CO}$ |
| | | 102 | $\mathrm{CrCl_3(CO)_3^+ \rightarrow CrCl_3^+ + 3\ CO}$ |
| Helium or butene or butane | [b]160 to 185 | 161 | $\mathrm{CrCl_3(CO)_2^+ \rightarrow CrCl_3(CO)^+ + CO}$ |
| | | 165 | $\mathrm{FeCl_3(CO)_2^+ \rightarrow FeCl_3(CO)^+ + CO}$ |
| | | 175 | $\mathrm{Fe_2(CO)_9^+ \rightarrow Fe_2(CO)_5^+ + 4\ CO}$ |
| Butene or butane | 260 | 261 | $\mathrm{Fe_2(CO)_9^+ \rightarrow Fe_2(CO)_7^+ + 2\ CO}$ |

[a] Calculated using the major isotope for each element.
[b] A number of parent peaks also occur in this range.

## CONCLUSIONS

It is concluded that the steps leading to the metastables are (1) prior attack of the heated cycloid envelope by water and hydrogen chloride mixtures leading to roughening of the wall (this step seems necessary since the metastables had not appeared previously, even when the same gas sequences were introduced into the instrument); (2) reaction of these roughened walls with carbon monoxide to form some type of adsorbed complex; (3) elution of carbonyls of iron, nickel, and chromium by helium, butene-1, or n-butane; and (4) decomposition products of these carbonyls which produced the observed metastable peaks.

It is noted that despite the difficulty the instrument is still capable of analyzing gases in the nanomole range. Procedures used to eliminate these problems if they reappear in the future consist of repeated sampling of carbon monoxide followed by sampling of helium as long as necessary.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, April 19, 1965.

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