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DETERMINATION OF CARBON MONOXIDE IN AIR BY TRIPLE QUADRUPOLE MA--ETC(11)

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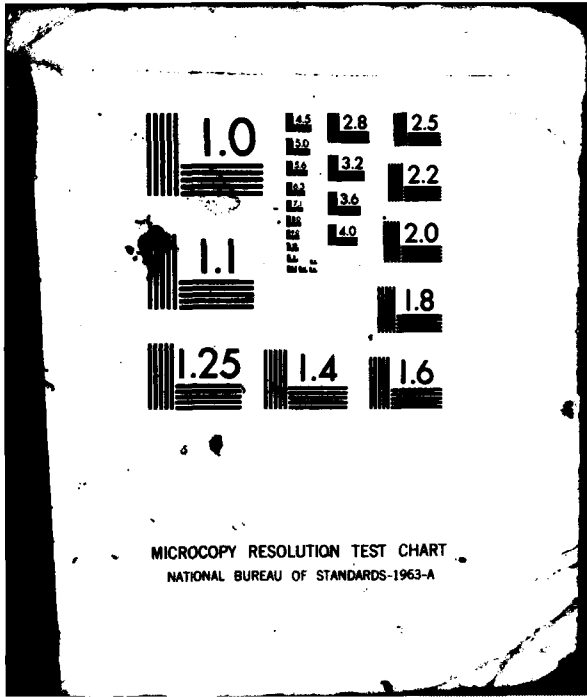
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DETERMINATION OF CARBON MONOXIDE IN AIR BY
TRIPLE QUADRUPOLE MASS SPECTROMETRY

by

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BRIEF

Carbon monoxide is determined in air at the part-per-million level in the presence of carbon dioxide and hydrocarbon. Quantitation is afforded by the addition of isotopically labeled CO.

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DETERMINATION OF CARBON MONOXIDE IN AIR
BY TRIPLE QUADRUPOLE MASS SPECTROMETRY

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ABSTRACT

Carbon monoxide has been determined at parts-per-million concentration in the presence of CO₂, N₂, and hydrocarbons by triple quadrupole mass spectrometry (TQMS). In this work, advantage is taken of the ability of TQMS to distinguish differing ions of the same mass. The first quadrupole mass filter selects m/z 28; these selected ions undergo collisionally activated decomposition in the RF-only quadrupole collision cell and the CO⁺ product ion at m/z 12 is mass filtered by the third quadrupole and detected. Quantitation of the CO concentration is achieved by the addition of a known amount of labeled internal standard, ¹³CO, which displays a fragmentation peak at m/z 13 when the first mass filter selects the parent at m/z 29. Side-by-side comparison with the m/z 12 peak from CO allows the determination of CO concentration to within 20% down to 10 ppm.

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INTRODUCTION

The application of mass spectrometry/mass spectrometry (MS/MS) to the analysis of mixtures is currently the focus of considerable study (1-4); several reviews have been published (5,6) which present a rather complete guide to the recent literature.

The isolation of components in a complex mixture by ionization and mass separation offers specific advantages over other techniques. For example, the component of interest is available continuously during the analysis, albeit at a lower flux, which contrasts the sequential delivery of the separated components by chromatography. For air analysis this is a distinct advantage since essentially continuous monitoring of a number of components is possible. For other samples the analysis is also extremely rapid (2), especially when compared to chromatographic retention times. In many cases little or no sample purification or derivitization is required (7,8).

The primary constraint in the use of MS/MS for mixture work is the necessity that the components of interest produce a strong molecular or other characteristic ion for selection and analysis. An ion which does not produce abundant molecular ion is difficult to analyze in a complex mixture. Also, abundant fragment ions may interfere with the analysis. Soft ionization techniques, for example, chemical ionization (9), field ionization (10) or field desorption (10,11) may be necessary to produce an abundant molecular or protonated molecular ion with little fragmentation. The triple (12) and double (13) quadrupole implementations of MS/MS have been described for several applications in mixture analysis (1,14-16); the unit resolution of both analyzer sections together with inherently high efficiency and sensitivity make the quadrupole MS/MS

ideal for analytical applications. In addition, since spectra generated by quadrupole MS/MS are in many ways similar to their MIKES counterpart, at least for electron impact generated ions (16), the considerable library of high energy CID and CA spectra may be useful for quadrupole MS/MS reference.

The application of mass spectrometry for the direct determination of trace amounts of carbon monoxide in air is a particularly difficult problem. Interferences from nitrogen at the same m/z preclude the use of low (unit) resolution instrumentation, although indirect methods (e.g., CO over CuO at $800^\circ \rightarrow \text{CO}_2$, then cryogenic trapping (17)) are available. Kambara et al. (18) have employed atmospheric pressure ionization to achieve impressive sensitivity for the determination of CO in N_2 but did not address the question of interferences from carbon dioxide and hydrocarbon. High resolution MS can easily differentiate the .011 amu difference between CO and N_2 at equimolar concentrations; however, the resolution required when the concentration ratio is as large as $10^6:1$ has not been attained.

The application of MS/MS, however, is ideally suited for the determination of CO in air. In the triple quadrupole implementation of MS/MS, the first quadrupole selects only those ions of m/z 28. Fragmentation of the N_2 component produces daughter ions at m/z 14, while for the trace CO component, the ion current at m/z 12 is detected.

EXPERIMENTAL

The triple quadrupole mass spectrometer used in this study has been described in detail (14). The instrument consists of, in series, an electron impact ionization source, an Extranuclear Labs quadrupole mass filter (Q1) an in-house designed and fabricated "RF-only" quadrupole collision cell (Q2), and a second Extranuclear Labs mass filter (Q3). Ion current is detected by a Galileo channel electron multiplier, amplified by a Kiethley #18000-20 picoammeter, and recorded on an H-P 7044-A X-Y recorder. The cross axial electron impact ionization source, designed and constructed in our laboratory for this work is more efficient than the commercial model it replaced and shows an apparent electron energy inhomogeneity of less than 0.25 eV based on appearance potential experiments (19).

The ionizing electron energy was set at 20 eV, and the emission current used was 50 microamperes. Repeller voltage was held at 10 V above the source block; sample pressure was 10 millitorr. Quadrupoles 1 and 3 offset voltages were -25 V while the axial energy (Q2 offset) was held at 33 eV, the optimum energy for the $\text{CO}^+ \rightarrow \text{C}^+$ transition studied. Target gas was 99.998% pure argon (Airco Industrial Gases, Southfield, MI, 48075), and controlled to 5×10^{-4} torr by a Granville Phillips model 216 flow controller.

Carbon monoxide and carbon dioxide gases were high purity, also from Airco; the isotopic standard (^{13}C O) was 99 atom % ^{13}C and purchased from Merck & Co. (St. Louis, MO 63116).

For these experiments, the ion of interest produced in the source and chosen for study (m/z 28 or 29) was selected by Q1; the selected ion was transmitted into the collision cell (Q2) where impact with

argon caused fragmentation. The positive focusing nature of the quadrupole collision cell allows little scattering loss (20) and thereby transmits nearly all CAD product ions to Q3 where they are mass analyzed and subsequently detected.

RESULTS AND DISCUSSION

A number of interferences can influence the ability to determine carbon monoxide in air by MS/MS. The first mass filter will select only ions of m/z 28 from the air matrix for study. Unfortunately, the major constituent of air, molecular nitrogen, is also seen at m/z 28. In addition, any hydrocarbon present larger than ethylene can have a $C_2H_4^+$ fragment at m/z 28. The most insidious interferent however, is carbon dioxide, which, at ambient concentrations produces an abundant CO^+ ion at m/z 28.

Interference from N_2

Certainly the easiest and most straightforward interference to eliminate is that from molecular nitrogen, even though it is present at some hundred thousand fold excess over carbon monoxide. The reactions:



are easily distinguished by quadrupole MS/MS. Figure 1 shows sensitivity and resolution easily attainable in the detection of 10 ppm CO in N_2 . Here, Q1 is set to pass mass 28; Q3 is scanned.

Interference from Hydrocarbon

In rare cases does the concentration of hydrocarbon in ambient air rise to appreciable levels. However, in an industrial or research environment it is possible that hydrocarbon concentration may rise to several thousand parts per million. Often, hydrocarbon produces fragments at m/z 28 with the composition $C_2H_4^+$. To ascertain the effect of this ion on the determination of CO, we chose as our contaminant ethane, which forms an abundant EI fragment ion at m/z 28. Performing CAD on this particular ion shows an ion intensity at m/z 12 of less than 0.5% of the base daughter peak (m/z 14). Together with fragmentation efficiency data for $C_2H_4^+$, this results in an absolute cross section of 0.0013 \AA^2 at 5×10^{-4} torr target pressure, as compared to 0.64 \AA^2 for carbon monoxide. In addition, the translational energy (E_{AX}) of the selected ion plays an important part in the efficiency for a particular transition (21). If the axial energy is chosen judiciously, ($E_{AX} = 33 \text{ eV}$, $V_{Q3} = -25V$) the hydrocarbon is attenuated further by at least a factor of two. A one thousand-fold excess of hydrocarbon ion at m/z 28 over the CO concentration is therefore required to produce equal signals at m/z 12.

Interference from Carbon Dioxide.

The most troublesome interference for CO determination by quadrupole MS/MS arises from the presence of carbon dioxide in air and other samples. At an ionizing electron energy of 70 eV, the cross sections for the production of CO^+ are virtually the same for both CO and CO_2 . Since the concentration of CO_2 in the atmosphere is 330 ppm, its potential for interference is significant.

Advantage is taken of the difference in collision cross section for CO^+ ions formed at low ionizing electron energies. The ionization

potential of carbon monoxide is 14.01 eV (22), while the appearance potential of CO^+ from carbon dioxide is 19.5 eV (23). While this circumstance is fortuitous, the more important criteria are the relative CAD product intensities at these low electron energies.

Figure 2 shows the ionization efficiency curve for CO^+ from CO by electron impact (labeled CO^+ under CO in figure), and the appearance potential curve for CO^+ from CO_2 , also by EI (labeled CO^+ under CO_2). Adjacent to these parent ionization efficiency curves are their respective daughter fragmentation efficiency curves for the reaction $\text{CO}^+ \rightarrow \text{C}^+ + \text{O}$ by Ar CAD. The cross sections for CO^+ formation from CO and CO_2 are within 10% at 70 eV electron energy; also, the cross section for the $\text{CO}^+ \rightarrow \text{C}^+ + \text{O}$ reaction is within 5% for the fragmentation of CO^+ from both precursors at this same energy. Therefore the processes shown in Figure 2 can all be normalized to 70 eV to facilitate comparison at lower energies. At 20 eV, the cross section for the m/z 28 \rightarrow 12 transition from CO_2 sample decreases by more than a factor of 10 compared to that at 70 eV while for carbon monoxide samples there is essentially no attenuation at 20 eV. The net result is that the CAD product intensity is reduced by a factor of four at 20 eV for carbon monoxide, while for CO_2 this intensity is reduced by 10^5 . Carbon dioxide interference can be reduced even more by further lowering the electron energy; however, this is done at great expense of carbon monoxide signal strength, which falls sharply below 20 eV.

This dramatic effect of the ionizing energy on the CO_2 interference is demonstrated by the simple but graphic isotope experiment shown in Figure 3. From an equimolar sample of CO_2 and

, a neutral loss ($M_{Q1} - M_{Q3} = 16$ amu) scan was
 The first analyzer (Q1) was scanned from m/z 27 to 30 while the
 analyzer (Q3) was scanned from 11 to 14. The peak at m/z 12
 from the CO_2 sample while that at m/z 13, from
 $^{13}C^+ + O$. The ion currents are nearly equal at 70
 eV; at 30 eV, the peak areas are in a ratio of about
 1:1. At 20 eV, essentially no contribution from CO_2 remains.
 The reasons underlying the reduction in the collision cross section
 from carbon dioxide at low electron energies appear to arise
 from an increased amount of vibrational internal energy as compared to
 singly ionized CO. These effects are the subject of a separate
 report (21).

Standardization of CO

The standard addition of isotopic CO enables the determination of
 carbon monoxide concentration in the sample. Care must be taken to
 ensure thorough mixing of the standard prior to analysis. With the
 collision energy at 20 eV and the axial energy at 33 eV, the mass
 filter is scanned to detect a neutral loss of 16. Samples from
 room air were spiked with approximately 1000, 500, 100, 50, 20, 10, and
 5 ppm each of CO and ^{13}CO ; all were spiked with 1000 ppm ethane.
 The differences in ion intensity of the sample and its
 standard were 20% at a maximum. For samples over 100 ppm, these
 differences were typically less than 10% (Table I).
 Figure 5.4 shows the neutral loss of 16 scan from m/z 10 to 15
 (per mass), of 20 ppm each of CO and ^{13}CO in room air, with
 1000 ppm ethane added. The peak at m/z 12 represents the analyte, m/z

13, the isotopic standard, and m/z 14, the $C_2H_6^+ \rightarrow CH_2^+ + CH_4$ transition from ethane.

The practical detection limit for our instrument in its current configuration is about 10 ppm. This limitation is imposed by the analog detection circuitry. Dual mode analog/pulse counting detection will be implemented soon and should improve the detection to below the interference limit.

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CREDITS

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Table I. Relative precision of CO determinations.

[CO] = [¹³ CO] ppm	Mean Deviation %
1000	3.8
500	5.8
100	8.1
50	15
20	18
10	15
1	37

CAPTIONS

- Figure 1: CAD spectrum of 10 ppm CO in N₂.
- Figure 2: Electron impact ionization efficiency curves for CO⁺; fragmentation efficiency curves for CO⁺ → C⁺ + O for CO and CO₂ samples.
- Figure 3: CO₂ and ¹³CO neutral loss of 16 scan, at 70, 30, and 20 eV electron energy.
- Figure 4: 20 ppm CO, 20 ppm ¹³CO in air neutral loss of 16 scan.

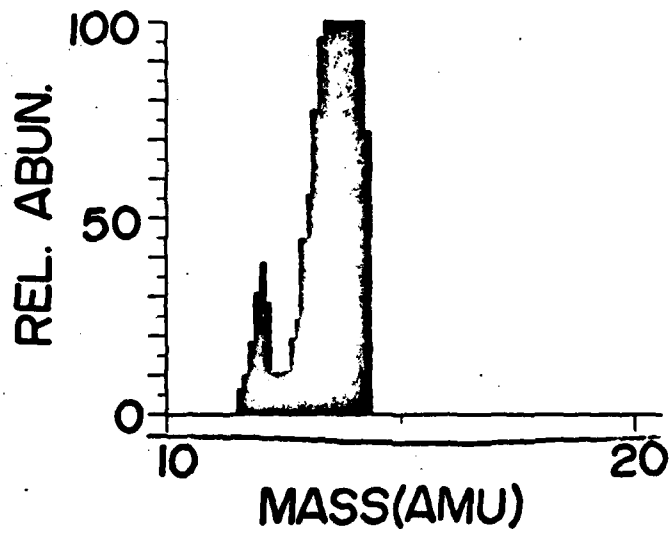


FIGURE 1

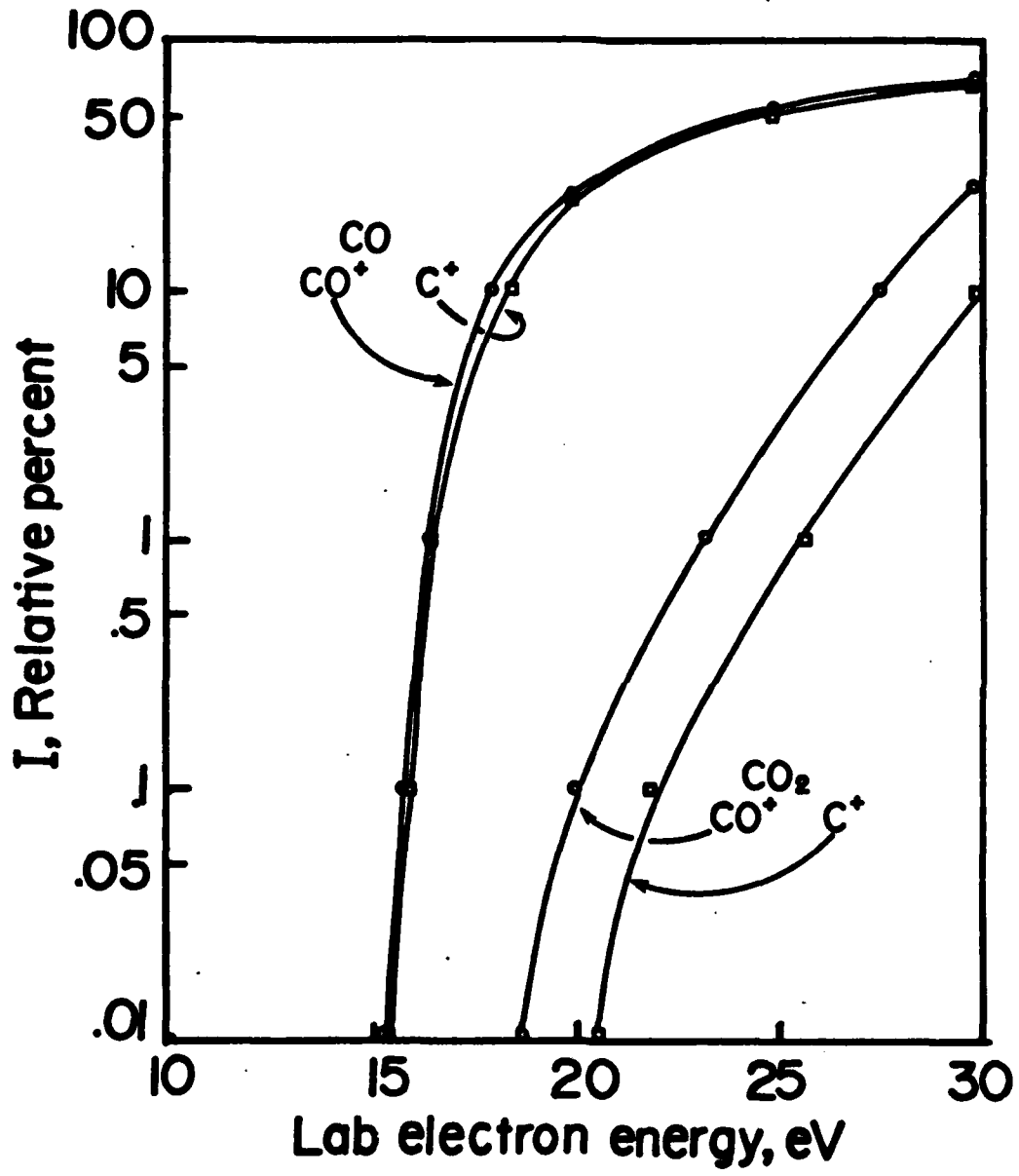


FIGURE 2

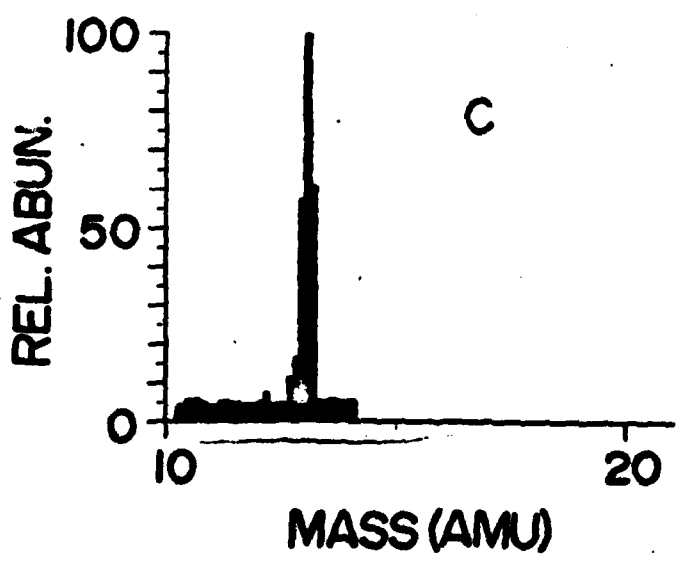
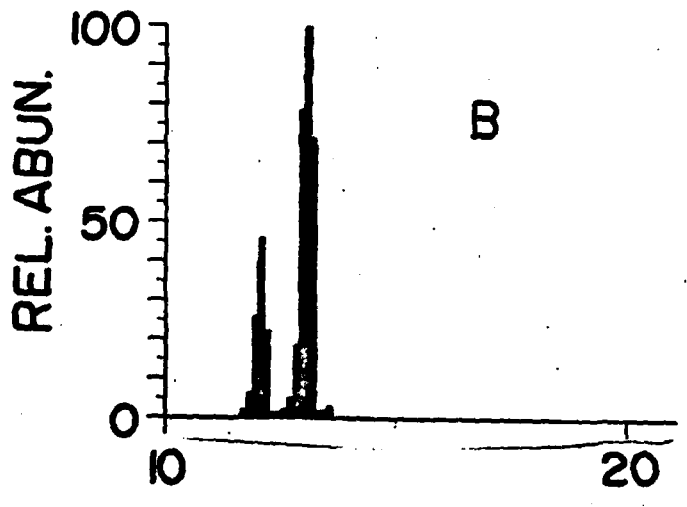
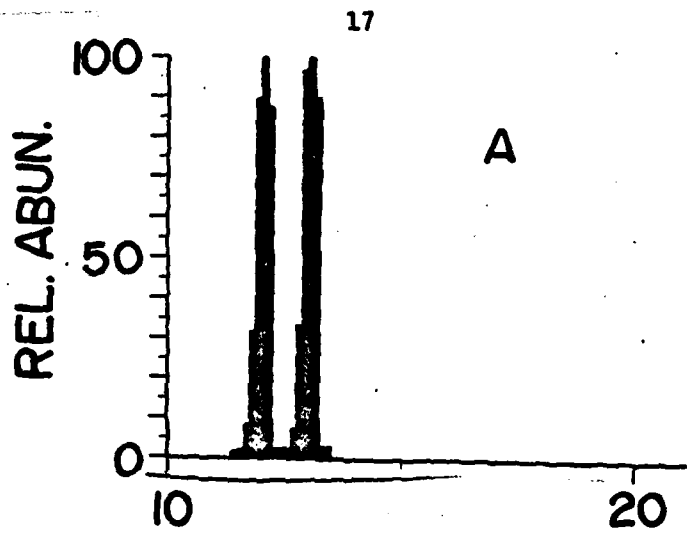


FIGURE 3

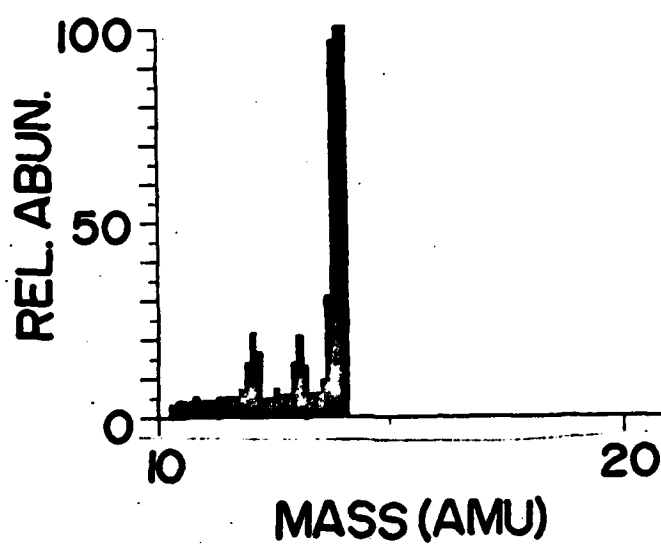


FIGURE 4