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Determination of Trace Amounts of Alkyls and Hydrides by Metastable Transfer Emission Spectrometry

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Experiments in which the newly developed analytical technique, metastable transfer emission spectrometry (MTES), was used indicate that this method can be effectively used to detect and measure small concentrations of metal and semimetal alkyls and hydrides in the gas phase. The molecules trimethylbismuth (TMB) and germane (GeH_4) were used for the prototype systems. However, many other molecules in these two classes can also be detected. Both TMB and GeH_4 have been measured in a flowtube device to concentrations of less than 10^7 molecules/cm^3, or an equivalent detectivity in the sample gas of better than 1 ppb. The flowtube detection device and its application to various problems are discussed. Other classes of compounds that should be detectable with our device are identified.

The recent development (1) of the new qualitative and quantitative measurement technique, metastable transfer emission spectrometry (MTES), has made it possible to detect various atomic vapors in a gas flow to concentrations of as low as 10^4 atoms/cm^3. This technique has been adapted, with no increase in experimental complexity, to permit the detection and measurement of many gas-phase molecules. The technique involves the mixing of a flow of sample gas, which contains traces of the molecule to be measured, with active nitrogen (2). The active nitrogen breaks apart the molecule and electronically excites one of its constituent atoms, e.g., Bi in the case of trimethylbismuth (TMB). Emission from the atoms is then monitored. The spectrum identifies the atom(s) present, and the intensities (I) of one or more of the emission lines are used as a measurement of the concentration of the emitting species:

$$I = K'(A) \qquad (1a)$$

or

$$I_{Bi} = K'_{Bi}(Bi) \qquad (1b)$$

In the case of TMB, K' and K'_{Bi} are constants. If there is no other source of the atom, its concentration is then, within limits, directly proportional to the concentration of the original parent molecule (M) present

$$(A) = K''(M) \qquad (2)$$

Thus, from Equation 1,

$$I = K(M) \qquad (3a)$$

where $K = K'K''$ is a constant. For TMB,

$$I_{Bi} = K_{Bi}(TMB) \qquad (3b)$$

The simple form of this equation has been verified over a large range of concentrations for several alkyls and hydrides. Limitations on the validity of Equation 3 will be discussed subsequently.

EXPERIMENTAL

The experimental setup is shown in Figure 1. The apparatus described in ref. 1 was used with two modifications. The furnace unit of the prior apparatus, which was used for vaporizing solid samples, was replaced by a system for handling gaseous species. In addition, the flowtube section was mounted horizontally and viewed end-on. A different and more accurate calibration method was also employed.

The sample gas, which contains small amounts of a molecule to be measured, is flowed at a known rate through a calibrated orifice, or through a capillary if smaller flows are needed, into the flowtube system. N_2 gas can be added to this sample flow, either before injection into the system or at the injection point by means of the outer coaxial jacket surrounding the sample injector. This N_2 flow is used especially when the sample flows are small, e.g., when the capillary is used, to positively sweep the sample into the reaction zone. Coaxial N_2 flow is initially adjusted to optimize the measured intensity for a given configuration and sample molecule. It is then adjusted as necessary throughout the experiment to compensate for changes in the sample gas flow, i.e., to keep the total flow constant in order to ensure that the mixing dynamics that occur downstream upon injection of the active nitrogen remain reasonably constant. The partial pressure in the flowtube, which is a result of the sample plus N_2 sweeping flow, is a sufficiently accurate diagnostic for adjusting the carrier N_2 flow. This partial pressure is typically about one third of the total flowtube operating pressure. Active nitrogen is also injected into the flow and accounts for the balance of the 2- to 5-Torr flowtube pressure. It is prepared by passing a flow of pure nitrogen gas contained in a 12-mm o.d. quartz tube through a 70-W microwave discharge upstream of the injection point. The discharge is confined to that portion of the 12-mm quartz tube surrounded by a McCarroll type cavity (3).

The glow that results in the mixing region and extends downstream is observed photoelectrically (RCA Model 1P28) through a monochromator. Normally, the glow consists primarily of atomic emission, with a weaker background of N_2 emission resulting from the Lewis–Rayleigh afterglow. Significant emission from other molecular species is seen only occasionally. The intensity of one of the atomic lines provides a qualitative measure (Equation 2) of the concentration of the parent molecule from which it was derived, if there are no other sources of that atom in the system and if the active nitrogen concentration remains relatively constant and unperturbed by the sample gas in the observation area. A simple calibration over the concentration range of interest in order to verify Equation 3 is all that is necessary to quantify the measurements for any particular experimental setup and sample gas.

For TMB, calibration consisted of the preparation of a dilute "standard" mixture of 1 part TMB in 10^4 parts of N_2. Further dilution gave irreproducible results. This mixture was then passed through the capillary (the orifice provided too large a flow) at a known rate, and the signal I_{Bi} was measured. The use of the known pumping speed of our system (3.25 L/s) enabled the TMB concentration in the observation area to be calculated. By means of Equation 3b, the calibration was thus effected. When such dilute mixtures and low flows of TMB were used, it was necessary to allow the system sufficient time to reach a steady-state equilibrium point before calibration data were taken. Experimentally we observed that with TMB, 15 min or more were necessary at very low flows. Although the TMB mixtures were made with N_2, such standard mixtures could also be made with other diluent gases, or with multiple trace samples in order to
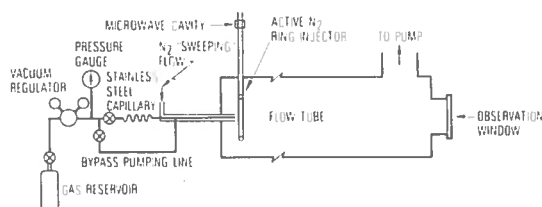
Figure 1. Flowtube device for detection of gas-phase species by MTES

duplicate more accurately the unknown gas that would ultimately be run in the system. The coaxial N_2 sweeping flow could similarly be replaced by other gases. Normally, when true unknowns are run, the trace substances are present in concentrations much smaller than $1:10^4$; hence, for maximum sensitivity, the larger flow afforded by the use of the orifice (0.005-cm radius hole) could be used. These larger flows would require no additional sweeping flow; thus, high sensitivity could be obtained with direct atmospheric sampling while maintaining the same system pressure.

RESULTS AND DISCUSSION

When the orifice is used, the flow is controlled by means of the upstream pressure (P_1). If $P_1 < 2P_2$, where P_2 is the downstream (flowtube) pressure, sonic flow conditions exist (4) and the flow rate through the orifice is directly proportional to P_1. For flow through the capillary, the flow rate is again controlled by the pressure, but the relation is more complex. Poiseuille flow normally develops (5), and the flow rate dN/dt of molecules through the capillary can be given with good accuracy by the expression

$$\frac{dN}{dt} = \frac{\pi a^4 (P_1 + P_2)(P_1 - P_2)}{16 \eta k T l}\left(1 + \frac{4\zeta}{a}\right) \quad (4)$$

where a is the inside radius of the capillary tube, l is its length, P_1 and P_2 are the respective upstream and downstream pressure, η is the viscosity of the gas flowing through the capillary, and

$$\zeta = \frac{2\eta}{P_1 + P_2}\left(\frac{\pi}{2}\frac{kT}{m}\right)^{1/2} \quad (5)$$

is the slip coefficient. The last term of Equation 4 (in parentheses) is a slip correction factor (5), which compensates for the fact that the velocity of the molecules flowing down the narrow tube is not zero at the walls. Reasonably long lengths of stainless-steel capillary tubing of $a = 0.005$ cm are readily available commercially; for these experiments, a relatively short length ($l = 15$ cm) is sufficient.

For convenience, Equation 4 may be rewritten as

$$\frac{dN}{dt} = \frac{\pi a^4}{16 \eta k T l} Z \quad (6)$$

where

$$Z = (P_1 + P_2)(P_1 - P_2)\left[1 + \frac{4\eta}{a(P_1 + P_2)}\right]\left(\frac{2\pi kT}{m}\right)^{1/2} \quad (7)$$

A steady flow of the sample gas, in this case 1 part TMB in 10^4 parts N_2, was established through the capillary. The flow was then shunted to a known volume at the same pressure (P_2). By the measurement of the time required for a small pressure rise in the known volume, it was possible to determine the flow rate (dN/dt). Measurements were taken for several values of P_1. dN/dt was then plotted vs. $Z(P_1, P_2)$ (Figure 2).

Clearly, a straight line resulted, demonstrating that the dependence of the flow on pressure given by Equation 6 is indeed valid. For this plot, P_1 was varied from 40 to 310 Torr. The initial concentration of the sample species in the flowtube observation zone is calculated from dN/dt and the pumping
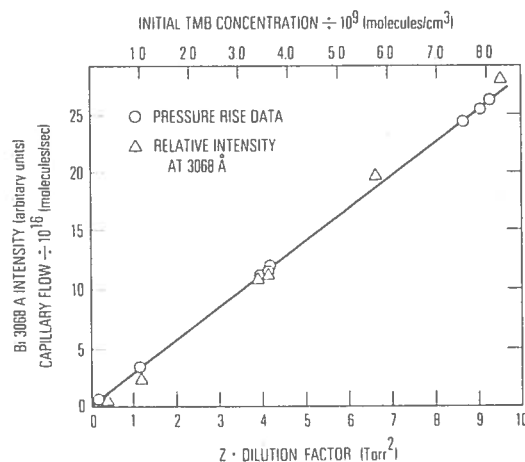

Figure 2. Capillary flow rate and intensity of Bi 3068-Å emission plotted vs. Z and initial TMB concentration
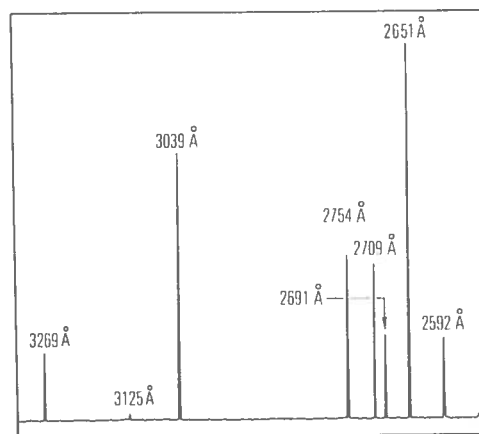

Figure 3. MTES spectrum obtained from trace amounts of GeH_4 mixed with active nitrogen

speed of the flowtube system.

Various flows of the TMB sample through the capillary and into the flowtube were established, and the signal intensity (I) produced by Bi emission at 3068 Å was measured to check the validity (i.e., the simple linearity) of Equation 3. I_{Bi} was plotted vs. Z. The result was again a straight line, as predicted, and, when the intensity scale was normalized at one point to coincide with Figure 2, the lines merged. Thus, at least for TMB, I_{Bi} is indeed proportional to the TMB concentrations, within the limits described previously, and Equation 3 holds. The range of linearity for TMB concentration measurements with our apparatus was from 10^{10} TMB/cm^3 to 10^7 TMB/cm^3. At higher concentrations, the plots showed some curvature, presumably because of active nitrogen depletion. With added difficulty, the measurements could be extended above 10^{10}/cm^3 in the current device by a careful calibration of the nonlinear portion of the curve. Signal-to-noise considerations prevented the measurement of concentrations below 10^7/cm^3. Lower concentrations could probably be measured with an optimized system with respect to f number, spectral slit width, and detector sensitivity. A concentration of 10^7 TMB/cm^3 was detected with a spectral slit width of 16 Å FWHM. The reduction of the slit width to 1.6 Å resulted in poorer detectivity by a factor of 14; the upper limit of 10^{10}/cm^3 remained, of course, unchanged.

Germane (GeH_4), a gas at room temperature, was also studied with the use of the MTES system. Dilutions of up to $2:10^5$ of GeH_4 in N_2 were used, and the intensity of the 2651-Å Ge emission line was monitored. A spectrum of the emission that results when active nitrogen is mixed with a gas flow containing trace amounts of GeH_4 is shown in Figure 3.
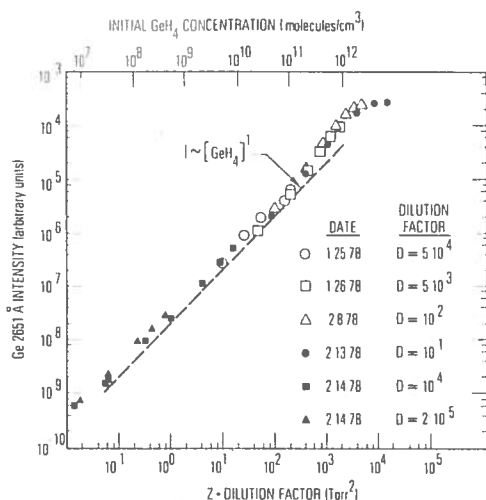
Figure 4. Intensity of Ge 2651-Å emission plotted vs. Z and initial GeH_4 concentration

Note that there is a relatively featureless background, clear of any significant spectral interferences. This featureless background is generally the case when MTES is used. If there are any spectral interferences, they are normally atomic lines resulting from other trace materials present. In a manner similar to that described for TMB, the validity of Equation 3 for GeH_4 was verified. These results are plotted in Figure 4, where a log–log format was used to accommodate the large dynamic range of the detection system. The emission intensity at 2651 Å is proportional to the initial GeH_4 concentration over a range of 5 orders of magnitude. The dashed line in Figure 4 was drawn with a slope of 1 and parallels the loci of data points.

Note that GeH_4 was detected at concentrations below 10^7 GeH_4/cm^3 or with about 0.1 ppb of GeH_4 in the sample gas flow. As before, this was achieved with a 16-Å spectral slit width. The effective upper limit of detection, determined as the highest concentration where the linear relation given by Equation 3 still holds, is approximately 10^{11} GeH_4/cm^3, as can be seen from Figure 4. With most trace molecules, this point was indicated by a bending over of the curve towards the x-axis, resulting from depletion of the active nitrogen. However, an interesting variation was observed with GeH_4. At concentrations between 10^{10} and 10^{11} GeH_4/cm^3, the intensity of the Ge 2651-Å emission line actually increased with the GeH_4 concentration at a rate increasingly faster than linear before finally saturating. Clearly, some secondary reaction was involved, but no specific mechanism is suggested at this time. The onset of saturation was indicated visually by a constriction of the pale yellow Lewis–Rayleigh afterglow and the appearance of new colors.

A number of other substances were put into the MTES system as "trace molecules", primarily to determine if they could be detected by means of the method; minimum and maximum detectable concentrations were not measured. All the materials tested were detected. Among them were AsH_3, PH_3, SiH_4, $Al(CH_3)_3$, $Ga(C_2H_5)_3$, and $Ge(C_2H_5)_4$. With the exception of PH_3, all of these materials yield clean atomic line spectra when added to active N_2. PH_3 and active nitrogen produce the PN $A^1\Sigma \rightarrow X^1\Sigma$ band system.

All of the "trace molecules" investigated thus far in the MTES apparatus exhibit a concentration region wherein the relation between the atomic emission intensity and the molecular concentration is linear, i.e., a region where Equation 3 holds. The exact kinetic sequence that occurs when a trace molecule is mixed with active nitrogen is not presently known; in fact, the reaction mechanism almost certainly differs for different molecular species (6, 7). It appears, however, that the general process involves the stripping down of the molecule to the central atom, probably by successive attacks on the N atoms present in the active nitrogen. Subsequent (one-step) excitation of the stripped atom by bimolecular collision with the $N_2(A^3\Sigma_u{}^+)$ would then account for the observed fluorescence (8, 9). It is unimportant whether the stripping reaction is first order or a more complex function of the active nitrogen concentration. Since MTES requires that the active nitrogen concentration be essentially constant, the analysis is valid as long as the overall kinetics are linear in the concentration of the sample molecule, which has been the case over a reasonably large concentration range for all molecules investigated thus far. As mentioned previously, however, deviations from linearity (other than simple saturation) have been observed with GeH_4. At high concentrations of sample gas, it is probable that secondary reactions with intermediate products of the stripping process may begin to play an important role. In any case, when working with a new molecule, the linearity expressed in Equation 3 should be verified empirically in the concentration range of interest.

The absolute accuracy achieved on a concentration measurement will depend on many factors, including the nature of the unknown, the background matrix in which it is embedded, spectral interferences, and, of course, the accuracy of the calibration standards. Reproducibility normally will be one of the prime considerations affecting accuracy. Similar flow conditions must be maintained in the device throughout an experiment, including keeping the active nitrogen production rate constant. Gross changes in the flow or composition of the sample and carrier gas must also be avoided, which is especially important if they contain species such as O_2, which can reduce detectivity both by quenching active nitrogen and by reacting with free atoms.

Throughout the experiments with TMB and GeH_4, the results were cross-checked, which included running identical concentrations on different days and comparing results obtained in the same experiment but using two calibration standards that differed in concentration by several orders of magnitude. Within the limits of applicability for the method, as described previously, it has been possible to achieve routinely an accuracy of ±15% (for 80% of the measurements) for all but the smallest concentrations.

CONCLUSIONS

Quantitative detection of a gaseous alkyl (TMB) and a hydride (GeH_4) at 1 ppb or less was demonstrated. Spectra were obtained that indicate that our process will be generally applicable to many molecules belonging to these two classes of compounds. In particular, tetraethyllead probably can be detected at concentrations well below the toxic level. Similar evidence exists in the literature that strongly indicates that a wide variety of metal carbonyls (10) and halides (11) could be detected and measured directly with our technique.

In a previous publication (1), we reported the detection of Bi atoms at a concentration of $10^4/cm^3$. It is probable that the reported sensitivity ($10^7/cm^3$) of the identical technique to trimethylbismuth is limited by the ability of active nitrogen to effect the decomposition of the metal complex. An auxiliary discharge or pyrolytic techniques applied to the gas flow containing the sample may improve the detectivity of the order of 10^2 to 10^3. As an alternative method, the sample may be passed through the same microwave discharge used to prepare the active nitrogen; however, design changes would be required to avoid the loss of metal downstream of the discharge.

Our technique looks promising for many applications. Three of the most obvious uses are: (1) as an alarm system for toxic gases of the types in question, (2) a method of analyzing feedstock gases used in the manufacture and doping of solid-state electrical components, and (3) a method of

analyzing combustion effluents.

ACKNOWLEDGMENT

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