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Applications of a Versatile Technique for Trace Analysis: Atmospheric Pressure Negative Chemical Ionization

by B. A. Thomson,* W. R. Davidson,* and A. M. Lovett*

The ability to use ambient air as a carrier and reagent gas in an atmospheric pressure chemical ionization source allows instantaneous air analysis to be combined with hypersensitivity toward a wide variety of compounds. The TAGA (Trace Atmospheric Gas Analyser) is an instrument which is designed to use both positive and negative atmospheric pressure chemical ionization (APCI) for trace gas analysis; this paper describes several applications of negative APCI which demonstrates that the technique is not limited to environmental monitoring. Examples are described which suggest that the TAGA can be used for the detection of illicit drugs and explosives, and for the analysis of breath or skin emissions, as well as for air pollution measurements. The applications are not restricted by the use of ambient air as a reagent gas; addition to the air carrier of various gases allows specific reagent ions such as Cl^- or Br^- to be generated. Furthermore, in certain situations pure gas carriers can be used to provide even more flexibility in the ion chemistry, with a short term absorber-desorber system used to transfer the sample from the ambient air into the ion source region.

The potential uses for APCI are expanding continuously as the understanding of the complex ion-molecule chemistry grows. This paper underlines the complementary relation between the development of new negative chemical ionization (NCI) techniques and practical applications using the TAGA system.

Introduction

This paper describes several diverse applications of negative chemical ionization with the Trace Atmospheric Gas Analyser (TAGA), an instrument which has been developed and engineered to take full advantage of the analytical capabilities of an atmospheric pressure ion source coupled to a mass spectrometer. The TAGA is designed to use real air, both as a reagent gas and as a sample carrier, and its unique potentials have been most fully realized to date in the field of ambient air monitoring. Chemical ionization at atmospheric pressure (APCI) results in high sensitivity to a wide variety of compounds, because the ion-molecule reaction rates are large, and the high-volume flow direct-air-inlet offers the ability to measure concentrations of gases in the air in real time ("instantaneously") at the parts-per-billion (ppb) to parts-per-trillion (ppt) level (*1-3*). One version of the instrument is mounted in a van and is able to sample air through a roof port and monitor pollutants either while the vehicle is stationary or in motion. This combination of mobility and instantaneous response allows point source plumes to be traced and concentration profiles outlined (*1*).

Both positive and negative ions can be generated in the ion source. Although a majority of the work on the TAGA has been performed using positive APCI, (because many of the environmentally important compounds of interest react with the positive ions in the TAGA ion source) several applications of negative APCI have been ex-

* Sciex Inc., 55 Glencameron Road, Toronto, Ontario, Canada L3T 1P2.

plored. Furthermore, the flexibility of the system has been expanded by adding various reagent gases to the air carrier in order to generate reagent ions which react with a very specific class of compounds, and in some cases by using a carrier other than ambient air. The first technique often results in an enhanced sensitivity toward the compound of interest, while achieving better detectability by eliminating interferences from other compounds which appear at the same mass. The second technique offers even more flexibility in optimizing the ion chemistry in the source, but requires special techniques for sample introduction. Both are discussed in the following sections, which illustrate the wide potential of negative APCI on the TAGA for applications in the environmental, medical, and public security fields.

Experimental

Figure 1 shows schematically the main features of the TAGA. The inlet system shown is designed to sample ambient air by drawing it through a 22-mm glass line, into the ion source region, at a flow rate which can be varied between 1 and 20 l/sec. A point-to-plane corona generates ions from the air as it emerges from the sample line; these reagent ions are pulled by the electric field (which imparts less than one-tenth of thermal energy to the ions) toward the vacuum orifice, and they react with trace neutrals in the air as they cross this space. The mixture of reagent and trace ions is focussed through a gas curtain in front of the orifice (which prevents it from being clogged with atmospheric particulates), and into the vacuum chamber. High speed cryogenic pumping removes the neutrals from the incoming beam, while the ions are focussed into the entrance of a quadrupole mass filter.

The features of the instrument which give it the unique capabilities of real-time ultra trace analysis are the following. (1) The high flow rate results in rapid sample clear-out time and virtually no memory effect, as well as nearly instantaneous (typically a fraction of a second) response to a change in concentration at the entrance. (2) Ion molecule reactions proceed very rapidly at atmospheric pressure if the energetics are favorable, resulting in efficient conversion of reagent to trace ions and thus high sensitivity. (3) Because the ions are thermalized at atmospheric pressure and temperature, the reactions are gentle, and the product ions are molecular or quasi-molecular in nature. This makes spectrum interpretation and trace identification particularly simple. (4) Water molecules, which cluster to the ions in the air, are stripped from the core ions by a patented system of combined gas dynamics and electric fields in the region downstream of the orifice. This declustering helps to maintain the simplicity of the mass spectrum.

This reaction region in the ion source is maintained in a steady state condition under the continual inflow of sampled air and flux of ions from the corona point of the orifice. The gas dynamics and chemical kinetics are such that for trace neutral concentrations of less than about 10 ppb,

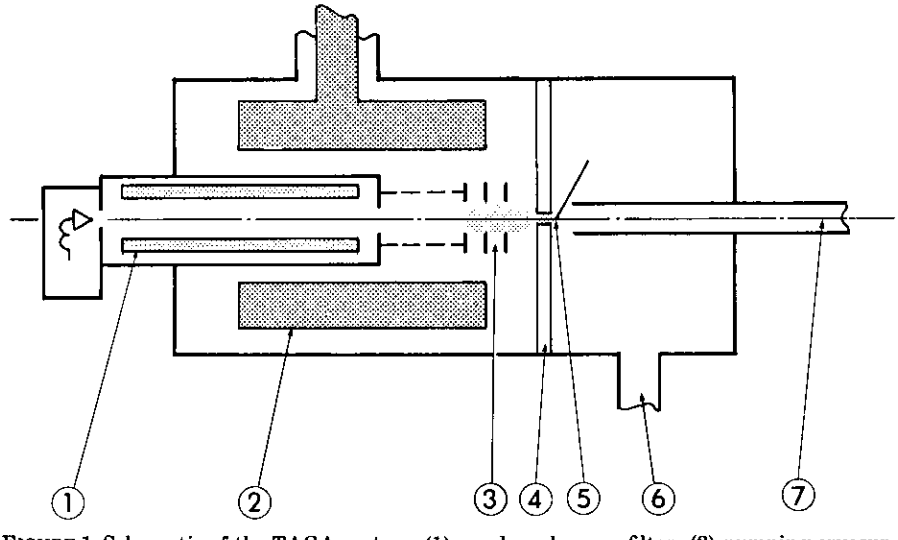

FIGURE 1. Schematic of the TAGA system: (1) quadrupole mass filter; (2) pumping cryosurfaces; (3) ion lenses; (4) interface module; (5) corona region; (6) to air pump; (7) ambient air inlet (glass pipe).

fewer than 10% of the reagent ions are converted to trace ions. This condition ensures that each ion molecule reaction is first order in trace neutral concentrations. Furthermore, in most cases only a small fraction of sample molecules are converted to ions; the result is that for concentrations in the ppb to ppt range, the instrument response (measured as ion signal at the mass of interest) is linear with the concentration of the species of interest, and independent of the concentrations of other trace neutrals. This is an important feature of the instrument which makes quantitative measurements of a complex mixture of gases (such as ambient air) relatively simple.

The APCI source with air as a reagent has some similarities with the standard CI source; however, there are enough differences introduced by the complexity and variety of the air consituents to make the ion chemistry in the TAGA unique. Ions are generated by electron impact in the corona, very close to the needle tip. The initial negative ions are primarily O_2^-, O^-, and OH^- (from the water in the air). These react very quickly to produce a mixture of O_2^-, O_3^- (from ozone generated in the discharge), CO_3^-, HCO_3^-, and NO_3^-. In normal ambient air these ions are hydrated with one to five water molecules (*4*); these hydrated ions are considered to be the reagents in the TAGA ion source. Reactions with trace neutrals (T) result in products of either T^-, if the trace has a higher electron affinity (EA) than the reagent, or $(T\text{-}1)^-$, if the trace has a higher gas phase acidity than the reagent.

The following examples are specific areas where the negative ion chemistry of the TAGA system has been utilized and in some cases modified, to measure trace gases concentrations in a variety of situations.

Environmental Applications

Sulfuric Acid Vapor Monitoring

Sulfuric acid is an environmentally important intermediate product of the oxidation of sulfur dioxide in the air. It plays a role in the acidification of precipitation and in the formation of atmospheric sulfate particles. Because it hydrates rapidly to a liquid form, it is present (in the gas phase) in only small concentrations in the air. Current methodologies for detecting sulfuric acid involve collection onto an adsorption medium, followed by laboratory analysis of the filter. However, this analysis is susceptible to interferences from continuing reactions among the sulfur compounds on the filter. The instantaneous response of the TAGA, and the ability to sample directly from the air make it particularily suitable for this application.

Since H_2SO_4 is a product of the oxidation of SO_2 (as well as a possible direct emission product from the same anthropogenic sources which emit SO_2), a real air monitoring situation will involve detecting H_2SO_4 in the presence of a larger concentration of SO_2. A mixture of SO_2 and H_2SO_4 was therefore introduced into the air carrier, and the response of the TAGA observed. The mixture of reagent ions (O_2^-, O_3^-, CO_3^-, and NO_3^-) reacts with the SO_2 and H_2SO_4 to produce SO_2^-, SO_3^-, SO_4^-, and HSO_4^- (Fig. 2*a*). When SO_2 was admitted alone, the same product ions were observed. It appears therefore that HSO_4^- is produced in the ion source by both SO_2 and H_2SO_4; this potential interference must be removed in order to measure H_2SO_4 in the presence of SO_2. This may be accomplished by converting the normal mixture of reagent ions to an ion which will react with H_2SO_4 but not with SO_2. One such reagent ion is Cl^-, which is generated when a chloride containing compound such as $CHCl_3$ is added to the air. When the same mixture of SO_2 and H_2SO_4 is introduced into the air carrier with Cl^- as a reagent, only products with a higher acidity than HCl are observed. Figure 2*b* shows the presence of Cl^- (the reagent ion), NO_3^- (undoubtedly from a trace of nitric acid which was present in the sulfuric acid), and HSO_4^+ from the sulfuric acid. No products are

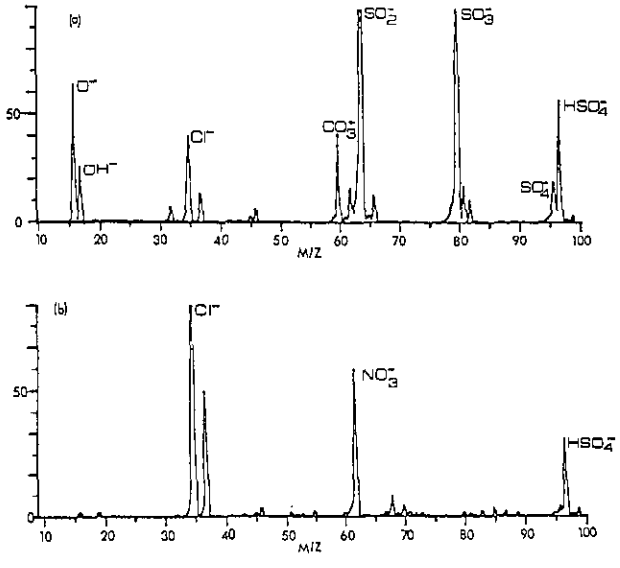

FIGURE 2. Mass spectra: (*a*) produced when a mixture of SO_2 and H_2SO_4 vapor is introduced into the air carrier; (*b*) produced when the same mixture is introduced with Cl^- as a reagent. NO_3^- appears to be formed from HNO_3 present in the H_2SO_4.

observed when SO_2 alone is introduced. The electron affinity of Cl is higher than that of SO_2, so that no charge transfer occurs from Cl^- to SO_2. With this "tailoring" of the ion chemistry, the real time monitoring of H_2SO_4 vapor (and other acid vapors) in the air is possible.

Monitoring Hexachlorobenzene in Ambient Air

Hexachlorobenzene (HCB) is a suspected carcinogen which is present as a contaminent in certain pesticides. Chlorinated aromatics have been observed to react with O_2^- in other ion sources (*5*) by nucleophilic substitution, to produce the $(M-Cl+O)^-$ product. Preliminary investigation of hexachlorobenzene in the TAGA ion source showed almost the complete absence of this ion, in spite of the known presence of O_2^- as a reagent. This may be due to the fact that the reagents are actually $O_2^-(H_2O)_n$, which are more stable than O_2^-, and which may also sterically hinder the reaction. Therefore, various synthetic gas mixtures (Ar, N_2, O_2, and CO_2 in various proportions) were tested as reagents by isolating the sampling line from the ambient air and using the mixtures as the carrier gas.

The phenoxide ion $(M-Cl+O)^-$ signal was observed to increase as CO_2 was added to carriers of either zero air or argon and the optimum condition for high sensitivity was reached with a carrier of pure CO_2. Identification of the active reagent ion is difficult due to the traces of O_2 and H_2O which remain in the CO_2. Up to the present time the justification for the use of CO_2 as a reagent gas to detect hexachlorobenzene has been strictly the empirically determined enhancement of phenoxide formation in CO_2 relative to ambient air.

In order to measure hexachlorobenzene in ambient air, a technique has been developed to allow collection from the air and transfer into a carrier of CO_2 for analysis, while maintaining close to real time capability. The technique is based on a short term preconcentrator, (Fig. 3) developed for monitoring PCBs in ambient air (*6*). A wire probe coated with OV-17 is exposed to the high volume flow of ambient air in the inlet line for a period of 60 sec, and is then transferred through a stopcock valve into the plenum region of the TAGA. In this position it is supported in a flow of CO_2 which is maintained continuously in the source region; the probe is heated by applying a voltage pulse, and the adsorbed vapors are driven from the probe surface into the carrier flow. Single ion monitoring at the mass of interest (one of the isotopes of $(M-Cl+O)^-$ for hexachlorobenzene) results in a transient signal of about 15 sec duration, as the HCB is desorbed. The integrated signal is proportional to the amount of HCB on the probe, and therefore, to the concentration which was in the air stream. This method allows 1-min averages of the HCB concentration in air to be measured every 2-3 min, with an ultimate detectability of about 30 ppt.

The contributions of the wire probe are therefore a preconcentration of the trace of interest, and the ability to use reagent gases other than air, while maintaining a turnaround time for each measurement which is short enough to be useful for *in-situ* air monitoring.

Public Security Applications

Explosive Detection

The presence of clandestine explosive devices can in certain situations be detected by the presence of vapors from the explosives in the air. It has previously been demonstrated (*7*) that the TAGA can detect the vapors from TNT, dynamite, and RDX in the air at concentrations of less than 1 ppt in real time. a more recent development has been the discovery that chloride ion attachment can be a very specific and sensitive type of chemical ionization technique for the detection

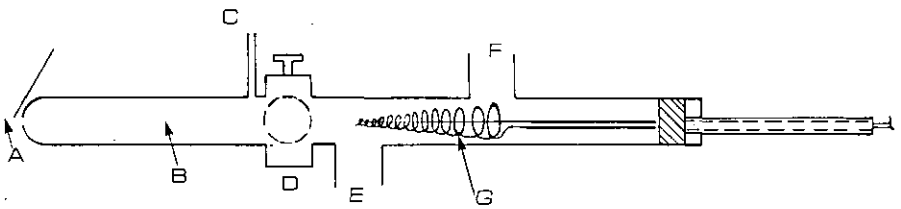

FIGURE 3. Wire integrator inlet system: (*A*) corona region; (*B*) desorb position; (*C*) nylon stopcock valve; (*E*) to air pump; (*F*) inlet for sampling air; (*G*) wire coil coated with OV-17, shown in the adsorb position. The integrator is supported on a nylon plug which can be moved back and forth in the sampling line, cycling between the adsorb and desorb positions.

Table 1. Chloride attachment.
$Cl^- + M \rightarrow Cl^- \cdot M$

M	Acidity, kcal/mole[a]	$-\Delta H^\circ_{Cl\text{-}Att}$, kcal/mole[b]	Response[c]
Methanol	43.2	14	−
Acetone	26.2	15	−
Phenol	16.2	27	+
Acetic acid	14.9	25[d]	+
Lactic acid	—	—	+
p-Cl-Phenol	9.8	27[d]	+
Nitroglycerine	—	—	+
HCl	0	24	+

[a] Acidity = $PA[M - H)^-] - PA[Cl^-]$.
[b] Enthalpy of chloride attachment reaction. Data of Kebarle (*10*).
[c] Plus (+) indicates an ion $Cl^-(M)$ was detected; minus (−) indicates that the attachment product was not observed.
[d] Estimated from data of Kebarle (*10*).

of nitroglycerine (a major component of dynamite).

Chloride attachment has been investigated in low pressure (1 torr) CI sources, and discussed in the literature (*8, 9*). Many examples which have been published have been tested in the TAGA ion source by generating Cl^- reagent ions and adding various neutrals to the carrier. Only a few have been observed as $Cl^- \cdot M$; Table 1 lists some of the compounds tested, along with their acidities and heats of formation of the chloride ion complex. the results suggest that only those molecules which are bound strongly to the chloride ion are observed. This in turn suggests that the more weakly bound complexes which are readily formed in other sources, must be dissociating in the TAGA either as they pass through the dry gas curtain in front of the orifice, or in the declustering region in the vacuum.

Attachment of Cl^- to nitroglycerine appears to be facilitated by the cooperative effect of the five acidic protons, as suggested in Figure 4. This figure shows a mass spectrum produced by a trace (a few parts per trillion) of nitroglycerine vapor in air, with Cl^- as the reagent. The specificity of the reaction $Cl^- + M \rightarrow Cl^- \cdot M$ is shown by the absence of other peaks in the spectrum. This lack of interferences, combined with the sensitivity and the isotopic ratio information makes this a very attractive technique for the detection and identification of nitroglycerine. In practical terms, the instrument resolution can probably be decreased in order to gain even more sensitivity, since the compound identification is so strongly supplemented by the ion chemistry. Bromide ion attachment to nitroglycerine has also been observed, and offers even more specificity in the chemistry, as well as moving the mass peaks ($Br^- \cdot M$) to even higher masses where potential interferences are fewer.

Illicit Drug Detection

Another practical application of the ability to sample ambient air in real time is the detection of illicit drugs by monitoring the vapor component in the vicinity of suspected personnel or containers. The situation is made difficult by the fact that many of the street drugs are hydrochlorides or salts, and therefore have low vapor pressures. In many real drug samples, however, minor amounts of more volatile compounds are present as diluents, contaminants or reaction biproducts, and one or more of these can be used as indicators of hidden drug samples.

One example under study is the use of acetic acid as a screen for heroin detection. Acetic acid forms the M − 1 ion ($m/z = 59$) in the source, and can be measured at concentrations of a few parts per trillion in the air. It is present in all heroin samples as a hydrolysis breakdown product. Table 2 lists the concentrations of acetic acid which have been measured in the head space of four seized heroin samples. Since acetic acid is present in many other preparations (aspirin, for example), it is not a very specific indicator for the presence of heroin. Work is therefore continuing to identify other breakdown products or diluents in illicit drugs which will be more specific indicators; preliminary indications are that heroin (base) is present in some samples and can be detected in real time.

Medical Applications

Monitoring Protein Metabolism in Real Time

Carbon dioxide is one of the major products of the metabolic breakdown of proteins in the human body. The metabolic process related to energy production can be monitored indirectly by

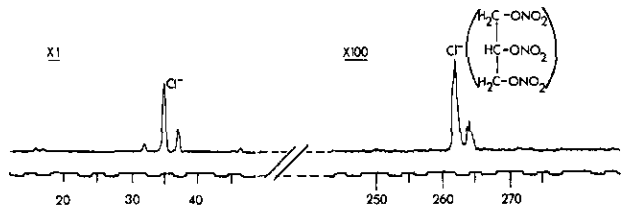

FIGURE 4. Two sections of mass spectrum of ambient air containing a trace (several parts per trillion) of nitroglycerine vapor, with Cl^- as a reagent. The mass scale is in atomic mass units (amu).

Table 2. Acetic acid concentration in the head space vapors of heroin samples.

Sample	Acetic acid concentration, ppm
1	255
2	174
3	134
4	188

measuring the ratio of $^{13}CO_2$ to $^{12}CO_2$ in the breath as a function of time after a subject has ingested a protein which is labeled with a ^{13}C atom in the carboxyl position. Standard techniques for such measurements often involve the use of radioactive isotope (^{14}C instead of ^{13}C), collection of samples for later analysis or extraction of body fluids for direct protein analysis. The use of the TAGA for direct analysis of breath for labeled CO_2 appears to offer the following advantages over the other current methodologies: (1) the analysis can be performed in real-time, allowing nearly continuous measurements, if so desired; (2) a nonradiactive isotope can be used; (3) no invasion of the body is required; (4) no sample collection, storage, or work-up is required.

In order to eliminate interferences from the 0.03% of CO_2 which is present in ambient air, the breath analysis is performed with a carrier and reagent gas consisting of 98% AR and 2% O_2. The subject exhales through a mouthpiece, and a splitter allows a small fraction of the breath to flow into the carrier with the rest being dumped to atmosphere. The carbon dioxide reacts to produce CO_3^-, CO_4^-, HCO_3^-, and HCO_4^-. The latter was chosen as the monitor for CO_2, since there is less interference at the mass corresponding to $H^{13}CO_4^-$ than is the case with the others. The reaction which forms this ion in the source is unknown; it has been observed as a product of ion-radical reactions in flames, and the reactions (*11, 12*) shown in Eqs. (1)-(6) are proposed as possible mechanisms for its formation in the TAGA in source:

$$CO_4^- + HX \rightarrow HCO_4^- + X \quad (1)$$

$$HO_2^- + CO_2 \rightarrow HCO_4^- \quad (2)$$

$$HO_2^-(H_2O) + CO_2 \rightarrow HCO_4^- + H_2O \quad (3)$$

$$CO_3^- + OH + M \rightarrow HCO_4^- + M \quad (4)$$

$$CO_3^- + H_2O + M \rightarrow HCO_4^- + H + M \quad (5)$$

$$HCO_3^-(H_2O) + M \rightarrow HCO_4^- + H_2 + M \quad (6)$$

On the basis of energetics reactions (2), (3), and (4) appear to be the most likely candidates; however, more investigation is required to definitely identify which is the most important reaction path.

Figure 5 shows an example of data collected by monitoring $H^{12}CO_4^-$ ($m/z = 77$) and $H^{13}CO_4^-$ ($m/z = 78$) during ten consecutive exhalations of 10 sec duration each. The data are collected on a PDP-8/m minicomputer system, and an average isotopic ratio is calculated automatically after each run of ten exhalations. Since the theoretical natural $^{13}C/^{12}C$ ratio is 1.08%, and a change of only a few percent is expected after ingestion of a labeled sample, a precision of four significant figures is required for accurate analysis. Careful control of the carrier gas purity and stability in the discharge region has allowed this precision to be achieved. Preliminary results of a feasability test with a real subject suggest that the technique is practical, and that the advantages of using the TAGA for direct measurement of isotopic ratios of metabolites in the breath can make it a valuable tool for clinical analysis as well as for reserach.

Monitoring Skin Emissions

The emission of vapors through the skin has received very little attention as a possible diagnostic indicator of various physiological malfunctions. The human body is no doubt a source of many trace compounds, either from direct skin emissions or from the surfaces of the oils and other liquids which coat the skin. Some are metabolic biproducts or end products, and may be use-

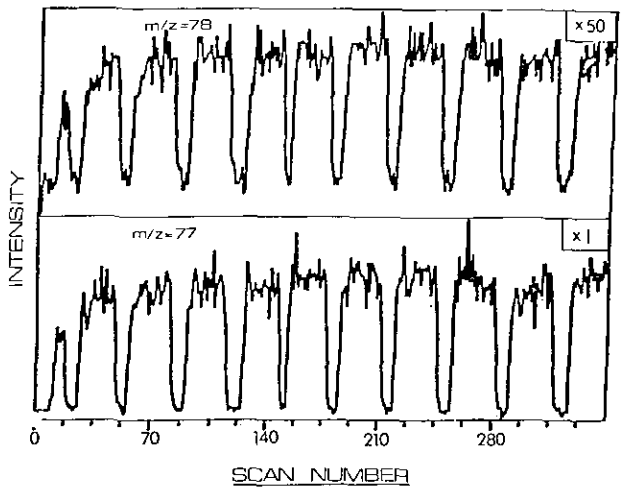

FIGURE 5. Selected ion monitoring of breath at masses corresponding to $H^{12}CO_4^-$ ($m/z = 77$) and $H^{13}CO_4^-$ ($m/z = 78$) during an experiment with ^{13}C-labeled leucine. Each peak represents an exhalation of several seconds (and scan numbers) duration.

ful as monitors of particular metabolic processes in the body. The TAGA system appears particularly suitable for such an application, since it has high sensitivity and can draw air from near the surface of any part of the body and analyse it in real time.

Figure 6*a* shows one example which has already been demonstrated. A section of the negative mode spectrum of room air is shown between 85 and 95 amu; Figure 6*b* shows the same section of the spectrum when a hand is held close to the inlet (3.5 l./sec of air is drawn in continuously). The two major peaks which appear are due to the $(M-H)^-$ ions of pyruvic acid (at $m/z = 87$) and lactic acid (at $m/z = 89$). The latter peak has saturated the chart recorder response, and so appears flat-topped. The identification of the peak at $m/z = 89$ as lactic acid has been further substantiated by checking the ratio of the $m/z = 90$ to $m/z = 89$ against the expected isotopic abundance ratio of lactic acid. Both pyruvic and lactic acid are known to be breakdown products of glucose metabolism. A more complete investigation is required in order to determine whether the measurement of emitted vapors has any diagnostic or reserach potential, not only for biochemical processes, but possibly for physical processes such as blood supply and delivery. A more elaborate sampling system than simply holding the inlet above the skin surface and drawing air into the system may eventually be required in order to use the full potential of the technique. However, even the qualitative information which can be obtained from direct skin "sniffing" may prove valuable to both the medical researcher and clinician.

Conclusion

This paper has demonstrated that when negative chemical ionization is applied in an atmospheric pressure ion source, an unprecedented combination of selectivity and sensitivity can be achieved. The ability to use ambient air as a carrier and reagent dramatically simplifies the application of such a technique to most real measuring situations, however, the TAGA is not limited to direct air analysis, nor to the use of normal ions generated in air or other pure gas mixtures as carriers. The examples which have been described show that real time ultra trace gas analysis can be useful in areas other than air pollution monitoring. New applications are being investigated continuously, and it is already clear that the use of negative ion APCI adds a powerful new dimension to the applications of the TAGA system.

The development work on sulfuric acid detection described in this paper was performed under contract to the Ministry of the Environment, Province of Ontario.

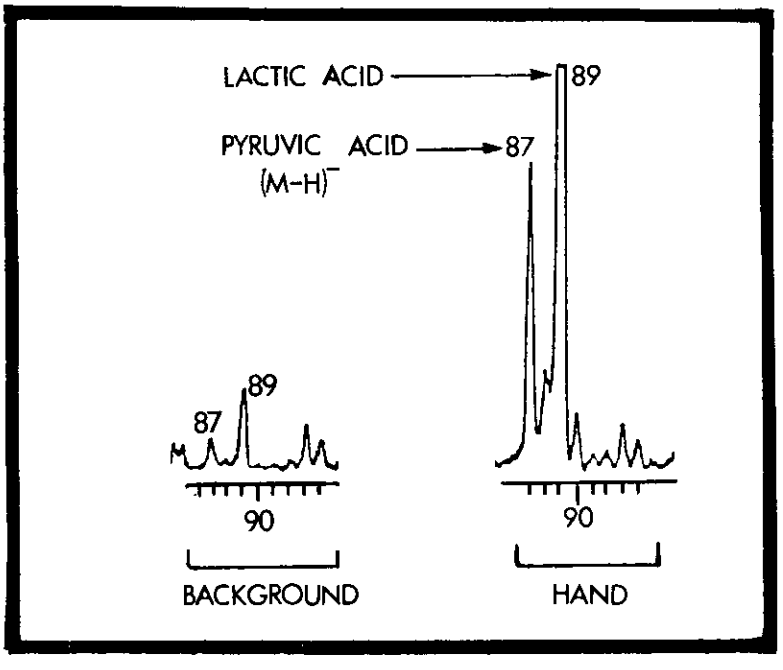

FIGURE 6. Two mass spectra of the region between 85 and 95 amu, showing a background of room air, and a response when a subject's hand is held in front of the inlet.

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