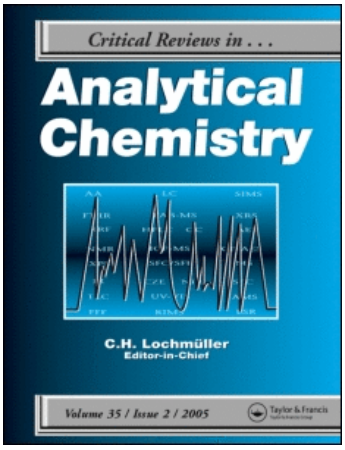


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# MOLECULAR EMISSION CAVITY ANALYSIS

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## I. INTRODUCTION

Molecular emission cavity analysis (MECA)[1,2] is a flame photometric technique which relies on a cool flame source to generate relatively broadbanded molecular emissions, such as $S_2$ and $BO_2$ and, therefore, directly opposes the trend towards hotter excitation sources and higher resolution monochromators required by the more conventional analyses based on atomic spectra. In practice, it has been found to be complimentary to atomic spectroscopic analyses, being able to determine elements (e.g., sulfur and nitrogen) having their atomic resonance lines in the vacuum UV region of the spectrum by the formation of molecules which emit in the visible and U.V. The advantages offered by the technique as well as the problems facing it are unique.

Two methods of MECA have developed concurrently, differing in the manner in which the sample is introduced for analysis. The first method is known as conventional MECA due to its similarity to the original discovery. It involves depositing the sample (microliters of liquid or milligrams of solid) into a cavity cut into the end of a rod. This probe is introduced to the flame, positioning the cavity in line with a detector. The second method, known as MECA-VAP, involves introducing the sample (up to several milliliters of liquid or grams of solid) into a reactor which generates a gaseous analyte which is swept by a carrier gas into a cavity in a probe permanently fixed in position in a flame.

In both methods, the cavity is positioned so that the flame enters and leaves the cavity smoothly. Transient emissions produced within the cavity are measured by a conventional flame emission spectrometer. The emissions are derived mainly from molecules, occur in characteristic and often quite broad wavelength regions, and are spectroscopically resolvable from each other only in certain cases. The intensities of emission at these wavelengths, using slits of 10 to 100 nm spectral bandwidths, are normally recorded on a strip-chart recorder.

In general, there is a reasonably wide difference in the applicability of each form of MECA and, therefore, in the direction each is naturally developing. This can be attributed to the different manner in which the analyte is vaporized from the sample prior to its emission. Problems have been noted which are limited to one form, and certain developments have been made which are particularly amenable to only one of these techniques, indicating that these are more than just variations on a theme. A comparison between these techniques, and between atom-based flame analysis in general, is made below whenever appropriate.



## II. METHODOLOGY

### A. General Considerations

*1. The Flame*

The flames used throughout MECA work thus far are relatively cool, hydrogen-rich flames, usually further cooled and made more rigid by the addition of nitrogen. The temperature of such flames is greatest at their outer edge because the main oxidant source is oxygen diffusing into the flame from the atmosphere. The composition of the flame varies across its width; the center is richest in unburnt hydrogen, molecular and atomic, while the edge is richer in oxygen-containing species, such as ·OH and the eventual product, $H_2O$. The concentrations of these species are governed by the equilibrium:

$$H\cdot + H_2O \rightleftharpoons \cdot OH + H_2 \qquad (1)$$

The concentration of electrons and ions is small, and the emissions generated in these flames are primarily chemiluminescent. Many can be attributed to direct interaction with hydrogen atoms, e.g.,

$$SnCl_2 + H\cdot \rightleftharpoons SnCl^* + HCl \qquad (2)$$

or to the result of third body action for recombination of hydrogen atoms:

$$H\cdot + H\cdot + M \rightleftharpoons M^* + H_2 \qquad (3)$$

Equation 3 provides up to 104 kcal $mol^{-1}$ of excitation energy.

Because of the limited number of species present, the flame itself produces little

emission in the visible or UV regions. The emissions are restricted to the OH band centered at 306 nm and a very weak continuum covering the visible region. This lack of flame emission allows relatively weak molecular emissions from added species to be detected, provided adequate efforts are made to prevent stray light from entering the detector.

The almost entire dependence of the generation of emitting species on radical reactions rather than on thermal excitation makes analysis using such cool flames particularly vulnerable to interferences by substances which change the radical concentration (including solvents), quench the emission, or prevent the analyte from forming an emitting species. The simple isolation of analyte from sample usually achieved in MECA is often able to circumvent such effects.

The above discussion relates particularly to the situation in the hydrogen-rich portion of the flame (normally the center), such as the well-known emissions from $S_2$ (for sulfur compounds) and HPO (for phosphorus compounds). Emissions which occur in the hotter outer edge of this flame, such as the green $BO_2$ emission from boron compounds, do not appear to be easily quenched and may, at least partly, arise from thermal excitation. In this flame region many broadbanded and continuum emissions (as well as atomic emissions) occur, which usually cannot be separated spectrally. In such instances, an isolation procedure for the analyte is required. The manner in which MECA readily accomplishes this and the reasons why it is considered the preferred means of utilizing flame molecular emissions analytically will be evident from the subsequent discussion.



### 2. *The Cavity as an Emission-Promoting Structure*

#### *a. MECA Introduction vs. Aspiration*

Several difficulties arise in attempting to introduce the analytical sample solution into cool flames by aspiration. Because of the low temperature, especially in the center of the flame, there is a great chance of the solid particulate which forms on evaporation of the aspirated droplet remaining intact, hence preventing the formation of the gaseous molecules required and thereby greatly limiting sensitivity and precision and giving rise to a situation where the total amount of solute present affects the response. With aspiration, the sample containing the analyte is introduced to the entire body of the flame, which may generate several emitting molecules in different zones of the flame (see the discussion on tin below), as well as emissions from other components of the sample. The solvent and the other components of the sample may alter the temperature and radical equilibria thereby changing (usually reducing) the intensity of the desired molecular emission and/or increasing the background emission and noise of the flame.

These problems are minimized using a cavity introduction of the sample. In conventional MECA the sample remains in the cavity, positioned in a selected zone of the flame and in line with the detector until the temperature is reached where vaporization occurs. This is usually at a time when the solvent has already evaporated. The MECA-VAP procedures employ reagents which are used to vaporize and transfer the analyte from the sample to the cavity, without the concurrent measurement of the solvent or other matrix components. In both techniques, the cavity environment can be controlled to promote the emissions from a selected group of emitting species. Further developments, which are described below, further improve the selectivity of response.

#### *b. Cavity Environment*

The environment of the cavity and its role in promoting the formation of certain emitting species can best be illustrated by examples of emitting species which exist under different flame conditions or zones. When tin(II) chloride solution is aspirated

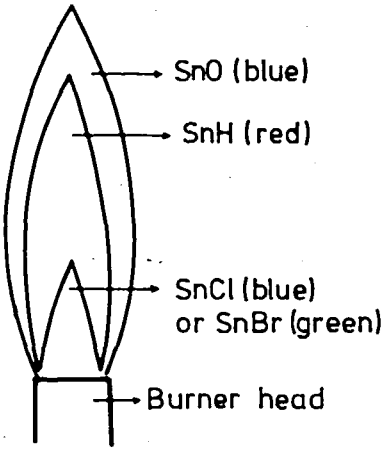



FIGURE 1. Cross section of a hydrogen diffusion flame showing the regions of different emitting species of tin, when tin(II) chloride or bromide is aspirated.



into a hydrogen diffusion flame, (i.e., hydrogen burning in air) three distinct zones can be observed, differentiated by the color emitted (Figure 1). The outer, more oxygen-rich edge shows a blue emission from SnO, the inner zone produces a red SnH emission, and a small central zone near the burner gives a blue-green SnCl emission.

Probable mechanisms for the formation of these emitting species are

$$SnCl_2 + H\cdot \rightarrow SnCl^* + HCl \quad (4)$$

$$SnCl + 2H\cdot \text{ (or } H_2) \rightarrow SnH^* + HCl \quad (5)$$

$$SnH + OH\cdot \rightarrow SnO^* + H_2 \quad (6)$$

$$SnH + O_2 \rightarrow SnO^* + OH \quad (7)$$

$$SnCl + OH\cdot \rightarrow SnO^* + HCl \quad (8)$$

Within the cavity a tin(II) chloride solution (introduced by conventional MECA) produces only an emission from SnCl,[3] indicating an environment of low temperature, low hydroxyl radical concentration and a modest concentration of hydrogen atoms, similar to the central zone of the flame near the burner. This remains the case even when the cavity is situated several millimeters above the burner head and is moved towards the edge of the flame, and when air is introduced to the body of the flame.

A similar situation exists for other metal halides, metal halide emissions being obtained[4] with a cavity introduction in cases (e.g., Cu[5], Pb, Mn, Fe, Ni) where only metal hydride, oxide, and/or atomic emissions are obtained by aspiration. This difference has been noted particularly where metal-halide bond strengths are fairly weak and, therefore, more easily broken in the more energetic body of the flame compared to the sheltered region of the cavity. In these cases, although a metal halide emission is obtained within the cavity, a considerable amount of the metal remains deposited on the walls of the cavity and can be encouraged to re-emit its metal halide emission by injection of the acid halide.

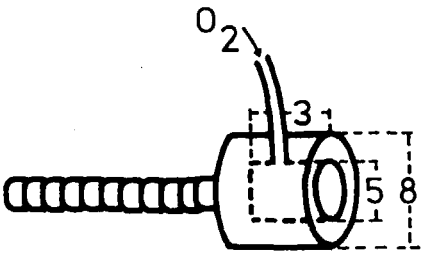



FIGURE 2. MECA oxy-cavity (dimensions in mm).

Such redeposition can be prevented and the metal halide emissions enhanced by introducing a small, steady bleed of hydrogen chloride gas to the cavity. The potential applications of this HCl cavity, particularly for metal analysis, are presently being investigated.[6] No metal halide emissions could be obtained from cadmium, silver, or mercury.

Halides, instead of metals, may be determined by introducing a metal such as indium, which forms a strongly bound metal halide-emitting species. This is required for halide determinations, since the halides have not been found to emit in the absence of such a metal.

The cavity conditions suitable for production of metal halide emissions are also suitable for the sulfur ($S_2$), phosphorus (HPO), selenium ($Se_2$), and tellurium ($Te_2$) emissions. Surprisingly intense atomic cadmium emission has also been found in this environment, thus allowing the determination of cadmium.[7] Atom formation is related to the ease with which the cadmium-halide bonds can be broken.

Elements such as arsenic, antimony, tin, boron, and silicon give no emissions when present in the cavity as a nonhalogen compound, but an emission is produced at the edge of the flame above the cavity. For tin, this is the oxide emission referred to above. Boron gives the green $BO_2$ emission in the flame above the cavity. The similar behavior of arsenic, antimony, nitrogen, and silicon indicates that their emitting species also contain oxygen. These emissions may also involve molecules that are normally excited and require relatively strong bonds in order to exist in the higher energy zone at the edge of the flame, but also involve continua, probably involving oxygen atom combination, such as

$$AsO + O \rightarrow AsO_2 + h\nu$$

All of these and other emissions may be induced within the cavity by supplying a small flow of oxygen into the cavity while it is in the flame by means of a stainless steel capillary tube. This modification, known as the "oxy-cavity[8] (Figure 2), has extended the range of MECA to include almost all the nonmetals and metalloids. The conditions within the oxy-cavity resemble those at the edge of the flame. With oxygen added to the cavity, $S_2$ and $Se_2$ emissions are not produced, PO rather than HPO emission is generated, and metal halide emissions are replaced by metal oxide or hydroxide emission. The hotter environment of the oxy-cavity encourages some atomic emissions, which have been used for the determination of lithium, potassium, sodium, and thallium.[9]

### *c. Composition of the Probe*

The composition of the probe, and specifically the cavity wall, is dictated with respect to several functions. As an emission-promoting structure, the cavity may be coated with an ingredient necessary for the formation of an emitting species, as is the case with an indium-coated cavity used for determination of halides ($X^-$) by generating

InX emissions.[10] This has most successfully been achieved by initially heating a piece of metallic indium in a copper-surfaced cavity until a bright red indium emission is observed and maintained for a few minutes, followed by pouring the excess molten indium out of the cavity. The bright layer of metallic indium coats the copper, presumably by forming an alloy. A modification involving embedding several layers of a fine copper mesh in a carbon cavity before treating with indium metal, gives a cavity having a prolonged life (>100 analyses), which has been used for the determination of percent concentrations of organic halides in lubricating oil. Copper[5] and tin[11] can be used in a similar way. It is important to realize that metal halide emissions can be obtained from many metal cavities such as those of stainless steel when strongly acidic halide solutions are present. These emissions might interfere with analytical measurements and therefore in such circumstances, there may be advantages in using probes fabricated from nonemitting materials, such as carbon,[12] with a pyrolytic cavity surface, a silica-lined steel cavity,[13] or aluminum.

Probes of copper,[5,14] tantalum, titanium, and zirconium[15] have been constructed but have not proved to offer any advantages over the normally used materials, i.e., 316 stainless, and hastelloy steel, carbon, silica-lined stainless steel, and the metal-halide cavities.



*d. Reflectivity*

Since some of the emissions which form within the cavity are reflected from the back wall of the cavity into the detector, changes in reflectivity of the cavity surface would be expected to alter the MECA response. Reflectivity, at a given wavelength, is a function of temperature, which may be quite complicated for certain materials.

Effects arising from variations in reflectivity are greater in conventional MECA. When a stainless steel cavity was introduced several times (for short periods only) into a hydrogen-based flame, the inner cavity surface gradually changed from straw-yellow to blue to deep violet, owing to the formation of an oxide surface of varying thickness (tempering colors). The reflectance variation at 384 nm was directly proportional to the measured $S_2$ emission intensity variation from a volatile sulfur compound. The decrease in measured intensity was as much as 50% in highly oxidized cavities. In order to obtain reproducible conventional MECA measurements, therefore, all cavities used should have the same reflectivity. Variations due to reflectivity changes are minimized by using an identical analytical procedure for each cavity, especially as regards the duration of heating in the flame. Such effects are not apparent with carbon or silica-lined cavities.

The effects of variation in cavity reflectivity have been noted in MECA-VAP (which utilizes a single cavity permanently positioned in the flame) only in the determination of ammoniacal nitrogen using a water-cooled aluminum oxy-cavity, and only at high amplification for the ammoniacal system. A gradual decrease in the background emission of the cavity was noted which was more rapid when a new aluminum probe was used. This was again attributed to the formation of an oxide surface in the cavity.

Provided the appropriate precautions are taken, variations in response due to changes in reflectivity are usually minimal. Their effects are included in the total variations of the procedures and applications described later.

*e. Temperature Considerations*

Two effects of cavity temperature are related to the cavity as an emission-promoting structure, namely, the incandescence of the cavity walls and a less obvious phenomenon first observed by Salet. The complicated relationship between temperature and reflectance at a given wavelength requires further study and is only mentioned briefly.

(1) Incandescence

In accordance with the laws governing black body radiation, the intensity of incandescent emission of the cavity material at a given temperature increases as the wavelength increases and the emissivity of the material increases. Thus, emissions measured at short wavelengths, e.g., $S_2$ at 384 nm, are virtually unaffected by the incandescent background emission from the cavity itself. Similarly, in MECA-VAP, where the temperature of the cavity is constant, no problems arise because either the temperature is controlled so that incandenscence is negligible or it achieves a constant intensity.

The only instance where incandescence becomes of concern is in a conventional MECA determination of an analyte that is difficult to vaporize and emits at long wavelengths. The determination of low concentrations of lecithin via its phosphorus HPO emission at 528 nm is such an example. For this analysis, a high-density carbon cavity with a pyrolytic surface is used because it has lower incandescence than a stainless steel cavity, or a high- or low-density carbon cavity without a pyrolytic surface. It is also important that the optics do not view the outer rim of the cavity, which reaches a higher temperature than the cavity interior and thus would made a large, steadily increasing background emission at long wavelengths.

(2) Salet Phenomenon

The discovery of the blue coloration of a hydrogen flame by a sulfur compound is attributed to Mulder.[16] Later, Barrett[17] found that different solids introduced into this blue flame itensified the blue color at the point where the flame contacted the solid. The intensity gradually decreased as the solid heated up. This enhancement, it was suggested, arose from sulfur contamination of the surface, which gradually disappeared with length of contact with the flame.

Salet[18,19] made a detailed investigation of the blue flame. He observed that the emission ($S_2$) was more intense in the cooler, inner regions of the diffusion flame, and was able to repeat Barrett's observations, using sulfur-containing solids. He found that a water-cooled platinum tube[20] enhanced the blue $S_2$ emission around the tube and eventually became covered by a thin layer of sulfur. If the tube was allowed to heat up (above approximately 500°C), no emission could be observed near the surface. Similar enhancements were achieved by a sheet of ice[21] or by allowing a current of chilled air[22,23] to cool the flame. This enhancement of $S_2$ (and HPO) emission by cool bodies, known as the Salet phenomenon, is utilized in MECA although no definitive work on its mechanism has been reported.

Applications of this phenomenon can be found in the development of the sulfur- and phosphorus-selective gas chromatographic detector.[24] Crider[25] showed how a borosilicate glass tube used as a flame sheath enhanced the $S_2$ emission near the (cooler) sheath wall, so that <1 ppm of $SO_2$ could be detected, whereas without the sheath no emission could be seen from <10 ppm of $SO_2$. Further investigations[26-28] of the solid sheaths identified sulfur- and phosphorus-containing deposits coating the sheath walls. Enhancements were not achieved if the solid sheath was replaced by an inert gas;[29] thus the effect is not one solely of the exlusion of air from the flame.

MECA emissions are also effected by the temperature of the cavity wall at the time of vaporization. This is indicated by the greater intensity and sensitivity produced by sulfur and phosphorus compounds vaporized at low temperatures compared to those of less volatile species (see later). This effect was first demonstrated by Bogdanski[1] and Belcher et al.[2] and confirmed by Calokerinos,[30] who measured the effect of cavity cooling on the emission intensities produced by introducing a constant flow of various vapors into the MECA cavity situated in a hydrogen-based flame. The $S_2$ emission from carbon disulfide was gradually increased as the cavity temperature decreased. However, the spectrum of the emission (Figure 3) did not appear to change either in

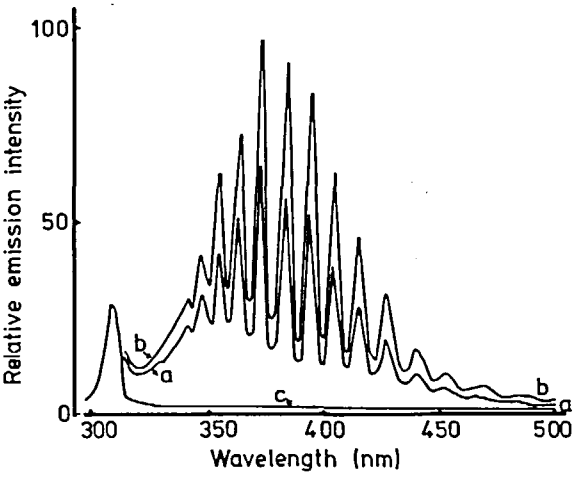



FIGURE 3. Sulfur emission spectra when carbon disulfide vapors from a $2.8 \times 10^{-4}$% (v/v) aqueous solution are introduced into (a) a hot (5 m*l* $H_2O$ $min^{-1}$), (b) a cold (100 m*l* $H_2O$ $min^{-1}$) water-cooled cavity (c) flame background. Flame = 4.2 *l* $H_2$ $min^{-1}$, 5.9 *l* $N_2$ $min^{-1}$, 25 m*l* $N_2$ carrier gas $min^{-1}$. Slit = 0.1 mm (1.7 nm).



wavelength or in the relative intensities of the various bands. It was concluded that the enhanced emission was not due to a change in the emitting species or to a redistribution of the energy among the various transitions. Furthermore, evidence for build-up of sulfur on the cooled surface was obtained.[31] $Se_2$ and HPO emissions are similarly enhanced.[32] It has been reported that a black selenium deposit on a cavity is required before a reproducible emission can be obtained in conventional MECA.[33] In contrast, emissions obtained from oxides (normally found at the edge of the flame on aspiration) including those of B, Si, N, As, Sb, and Sn, as well as CH and $C_2$ emissions obtained from triethylamine,[30] were all increased by decreasing the cavity cooling, as would be expected from a thermal excitation process. PO emission behaved similarly, showing the reverse behavior to that found for HPO. Thus, the Salet enhancement appears to be restricted to certain emitting species, namely $S_2$, $Se_2$, HPO, and various metal halides.

A necessity for the formation of the sulfur deposit before optimal enhancement is achieved has been noted. This suggested that the surface may be actively involved in the formation and excitation of emitting $S_2$ species, making these reactions more efficient. The cooling enhancement may also be attributed to lowering the temperature of the flame in the vicinity of the surface and greatly decreasing the radical concentration necessary for excitation. This may be the prime reason for enhancement of many of the metal halide emitters which are known to have easily dissociated bonds. The above effects may well be a means of differentiating between chemiluminescence and thermally generated emission, if proper considerations are given to the bond strengths of the molecules involved. These speculative considerations can be supported to a degree, but much more work is needed for clarification.

In conventional MECA, the cavity temperature at which a compound vaporizes to generate an emission is governed by the chemical and physical properties of that compound. Thus, Salet enhancement would be most important for those compounds which volatilize readily, but would have a lesser effect on less volatile compounds. In order to circumvent this discrimination, the vaporization process and the emission process

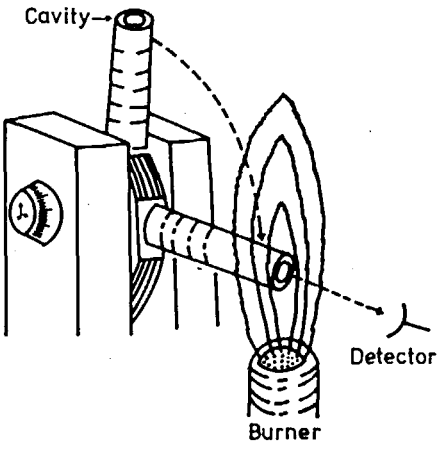



FIGURE 4. Rotatable cavity holder. (From Belcher, R., Bogdanski, S. L., Knowles, D. J., and Townshend, A., *Anal. Chim. Acta*, 77, 53 (1975). With permission.)



can be physically separated, as is achieved in MECA-VAP. The volatilization process results from a controlled chemical reaction, and the gases are fed to a cavity at an optimal temperature, either for promoting a Salet enhancement (i.e., a low temperature) or for promoting oxide emissions (i.e., a hot cavity). The optimal temperatures for some emitters have been observed to increase in the order $S_2$ < InX < HPO < $Se_2$ < $Te_2$ < CH, NO, PO < $BO_2$ < SiO. The temperature may be decreased by water cooling or by using a cavity material of greater thermal conductivity. Alternatively, it may be increased by increasing the flame temperature or flame size, which increases as the hydrogen flow increases; this has led to a decreased $S_2$ emission[30] and increased NO[30] and SiO[34] emissions.

### *f. Size and Shape*

The best size and shape for a cavity is related to the size, composition, and shape of the flame used, and thus to the burner system. It is also dependent on the angle of cavity introduction into the flame, and its horizontal and vertical position in the flame. In addition, efficient viewing of the cavity by the detector must be achieved. The interaction of so many independent and dependent variables makes it difficult or unnecessary to suggest an optimal cavity size or shape. That normally used is 5 mm in diameter, having a 50-$\mu\ell$ volume, formed by boring with a conventional drill. Osibanjo[15] suggests that a cavity 8 mm in diameter × 5 mm deep is preferable when using an Evans Electroselenium 240 spectrometer burner with an emission head. koumtzis[35] describes a particular shape of cavity offering advantages for holding solids. Generally, it has been noted that increasing the volume of the cavity extends the linearity of calibration at the expense of a poorer limit of detection for HPO and $S_2$ emissions.

## B. Conventional MECA

The original system, designed for direct addition of liquid or solid samples to the cavity, is known as conventional MECA. A few microliters or milligrams of sample are introduced into the cavity at room temperature. The probe containing the cavity is moved (usually by rotation) so that the cavity is introduced rapidly and reproducibly into the desired position in the flame (Figure 4). The probe is tilted a few degrees below the horizontal to allow nonturbulent access of the flame into the cavity. The optics

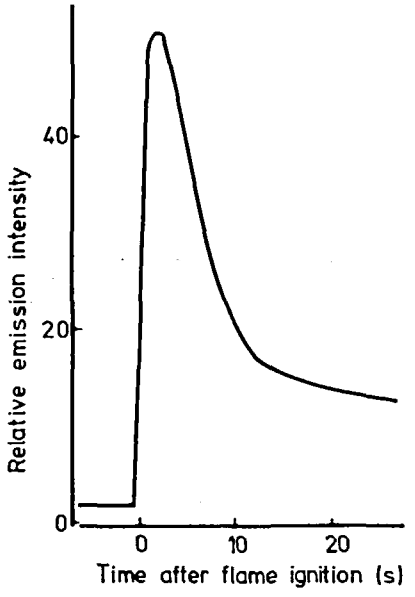



FIGURE 5. $S_2$ emission-time profile at 384 nm from 2 $\mu l$ of 10 ppm sulfur as aqueous thiourea.



are designed to view only those emissions which are generated within the cavity. Restriction of the emissions to within the cavity is readily achieved by appropriate adjustment of the conditions (see below). A typical response from a sulfur-containing compound is shown in Figure 5.

Once in the flame, the cavity temperature gradually increases. The rate of increase and ultimate temperature reached depends on the flame conditions, the position of the cavity in the flame, the size and composition of the probe, and the effectiveness of the probe holder as a heat sink. Typical heat-up rates for different cavity materials are shown in Figure 6. When the heat-up rate is required to be slow, water-cooling of the cavity can be used (Figure 7).

When the cavity containing a few microliters of a sample solution enters the flame, several processes occur:

1. Solvent evaporation, unless previously evaporated[12,36]
2. Analyte vaporization, possibly as a result of decomposition
3. Formation of emitting species from analyte vapor
4. Excitation
5. Emission or other de-excitation process

Although these events normally occur in sequence, occasionally they occur concurrently. A volatile analyte may be vaporized along with the solvent and, in this case, the nature and amount of solvent will effect the ultimate response. The vapor phase events, i.e., the formation, excitation, and emission, occur on a much faster time scale than the vaporization processes which are measured in seconds, and thus the response time is primarily controlled by the vaporization of the analyte. The analyte vaporization time is a function of cavity temperature. As this time also varies considerably between compounds, it provides an important qualitative aspect to the technique.

By relating the composition and temperature of cavities in various probes to the

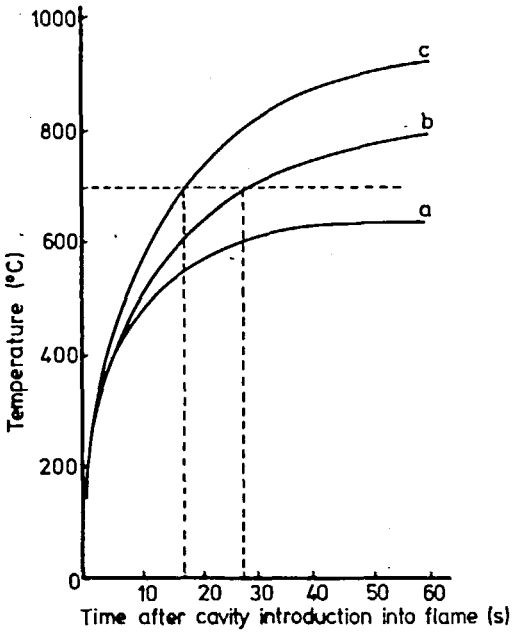



FIGURE 6. Increase in temperature of various cavities: (a) carbon (b) stainless steel, (c) stainless steel with ceramic insulation to reduce heat flow from cavity, after introduction into the center of an hydrogen-nitrogen-air flame (6.0 *l* $H_2$ $min^{-1}$, 6.0 *l* $N_2$ $min^{-1}$, 4.5 *l* air $min^{-1}$).

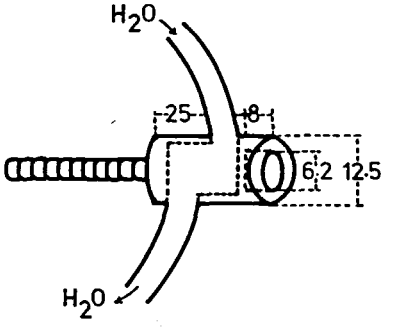



FIGURE 7. Water-cooled, stainless steel or aluminum alloy cavity (dimensions in millimeters).

response obtained for various compounds, it has been possible to suggest several mechanisms by which the vaporization of the analyte may occur. They can be summarized as follows:

1. Boiling
2. Sublimation
3. Thermal decomposition
4. Reductive breakdown
5. Catalytic breakdown

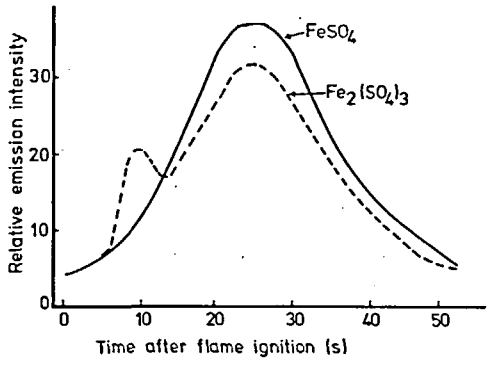



FIGURE 8. MECA responses obtained for iron(II) and iron(III) sulfates.

As the temperature of the cavity material increases following flame introduction, analyte vaporization proceeds by the mechanism which occurs at the lowest temperature under the appertaining conditions.

For analytes vaporizing by boiling (e.g., many organic sulfur compounds and sulfuric acid), sublimation (e.g, iodine, selenium dioxide), and thermal decomposition (e.g., thiourea, sulfates of iron(II), manganese(II), and sodium), the time taken to achieve maximum emission intensity after introduction to the flame ($t_m$) is directly related to their boiling, sublimation, and thermal demposition temperatures. Such compounds give emissions which appear in an order that remains unchanged by altering cavity material, external cooling, or flame conditions. The $t_m$ values and emission intensities, however, change because of the change in heating rate when these parameters are changed.

The $t_m$ values for the $S_2$ emission produced by the sulfates of copper(II), silver, cadmium, and mercury cannot be correlated with their temperatures of thermal decomposition, but can be correlated with increasing redox potential of the metal ion, suggesting reductive breakdown of the metal sulfates. In addition, the emissions occur earlier when a stainless steel cavity is replaced by a pyrolytic-carbon-coated carbon cavity, suggesting that carbon is participating in the reductive process more effectively than the components of steel.

The two mechanisms can be summarized as:

$$Na_2SO_4(s) \xrightarrow{\Delta} Na_2O(s) + SO_3(g) \quad (9)$$

$$CuSO_4(s) + 2H\cdot(g) \text{ (or } (C(s)) \rightarrow Cu(s) + SO_3(g) + H_2O(g) \text{ (or } CO(g)) \quad (10)$$

both followed by

$$SO_3(g) \rightarrow S_2^* \rightarrow S_2 + h\nu \quad (11)$$

Iron(III) sulfate shows two successive emission peaks (Figure 8).[1] The first peak is attributed to reduction of iron(III) sulfate to iron(II) sulfate by the flame with release of sulfuric acid vapor:

$$Fe_2(SO_4)_3(s) + 2H\cdot(g) \rightarrow 2FeSO_4(s) + H_2SO_4(g) \quad (12)$$

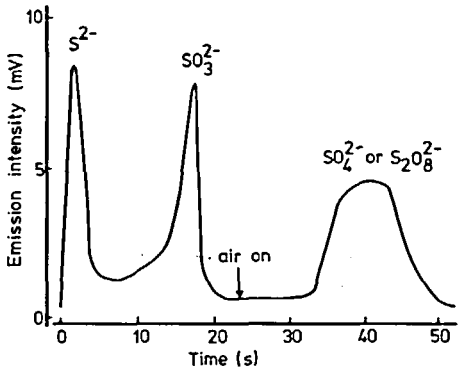
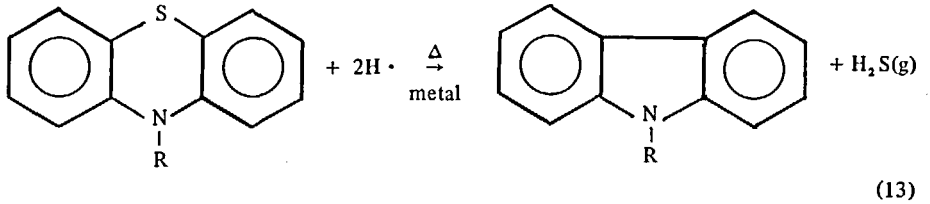



FIGURE 9. MECA response in a stainless steel cavity with silica liner (flame = 1.70 *l* $H_2$ $min^{-1}$, 4.0 *l* $N_2$ $min^{-1}$) in the presence of $1 \times 10^{-2}$ *M* diammonium hydrogen phosphate from 5 $\mu l$ of 10 ppm S as sodium sulfide + 16 ppm S as sodium sulfite + 30 ppm S as sodium sulfate or ammonium peroxodisulfate. (From Al-Abachi, M. Q., Belcher, R., Bogdanski, S. L., and Townshend, A., *Anal. Chim. Acta*, 86, 139 (1976). With permission.)



The second peak has the same $t_m$ as that of iron(II) sulfate and is attributed to a thermal decomposition process similar to that given for sodium sulfate (above). Repeated introduction of the iron(III) sulfate solution and MECA treatment results in a decrease in the first peak and a corresponding increase in the second peak, due to a deposit of iron(II) oxide which builds up in the cavity. This essentially reacts with the sulfuric acid released at the time of the first peak to form the more refractory iron(II) sulfate. This situation is eliminated by acid cleaning the cavity after each injection of sample. Only the first peak appears at a faster rate and is enhanced when a carbon cavity is used in place of the stainless steel cavity.

The only case where the situation is reversed has been attributed to catalytic breakdown, e.g., a substituted phenothiazine vaporizes and emits much quicker in a stainless steel cavity than in a carbon cavity. This is believed to be due to a catalytic effect of the metals in the steel:[12,37]




(13)

Although these speculations are difficult to confirm, they have given some appreciation of a area where a new technological development is needed and the important role played by the cavity material.

Because compounds having a common element are likely to have different $t_m$ values, it is possible to differentiate between such compounds in admixture, provided there is sufficient difference between the $t_m$ values. Thus, binary[38] and certain ternary mixtures of sulfur anions (for example, sulfide, sulfite, and sulfate[141]) can be determined simultaneously by measuring their resolved MECA peaks (Figure 9). In order to maximize

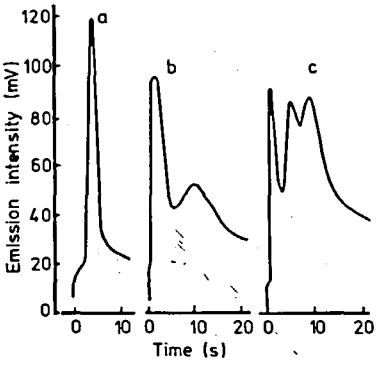



FIGURE 10. Effect of water cooling on the MECA response from a mixture of trimethylphosphate (100 ppm P); triphenylphosphate (50 ppm P) and di-(2-ethylhexyl)phosphate (50 ppm P); water flow: (a) 10 m$\ell$ s$^{-1}$; (b) 1 m$\ell$s$^{-1}$; (c) nil. (From Belcher, R., Bogdanski, S. L., Osibanjo, O., and Townshend, A., *Anal. Chim. Acta*, 84, 1(1976). With permission.)



the difference in $t_m$ values, a slow heat-up of the cavity is required, as is achieved with a water-cooled cavity. However, it should be appreciated that the maximum temperature achieved by efficient water-cooling may be below the temperature required to decompose and/or volatize some compounds. For example, in an attempt to resolve each component of a mixture of trimethylphosphate, triphenylphosphate, and di-(2-ethylhexyl)phosphate, by using a water-cooled cavity,[39] no emission was generated by the last two components (Figure 10a) because the compounds had not volatilized. On removing the water-cooling, the HPO emission of the second and third components appeared. This led to the development of a crude temperature programming arrangement in which the cooling water flow rate was gradually slowed during the experiment. The result is shown in Figure 10.

The oxy-cavity can be used in conventional MECA, provided external cooling is also employed. This has required the less convenient procedure of repeatedly shutting the flame off between sample introduction (or sliding it away from the cavity), since a stationary probe is usually necessary. These modifications are now mainly used with the MECA-VAP system described in the next section.

### *1. Experimental Parameters in Conventional MECA*

#### *a. Cavity Material*

As has already been discussed, the cavity material greatly influences vaporization of the sample. The thermal properties, such as heat capacity and thermal conductivity, as well as the contract between the cavity probe and the holding assembly (which acts as a thermal well) are important since they affect the temperature-time relationship, i.e., the rate of heating and ultimate temperature reached. This in turn affects the response. The cavity material may also have certain chemical effects, as discussed earlier.

#### *b. Cavity Position in the Flame*

The MECA flame is obtained from hydrogen diluted with nitrogen burning in air, and sometimes also contains added air. The oxygen from the air diffuses slowly into

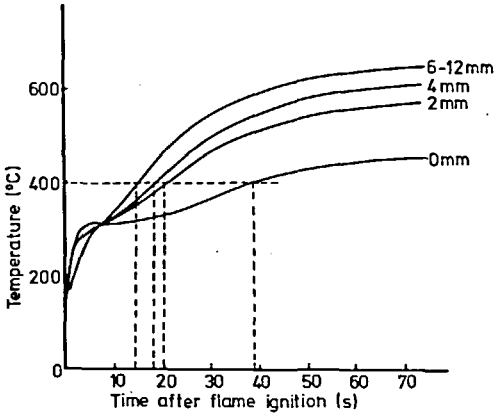



FIGURE 11. Increase in temperature of a stainless steel cavity positioned at various distances into the flames measured from the front of the cavity to the edge of the flame away from the detector. The diameter of the flame is 12 mm. Flame = 2.9 *l* $H_2$ $min^{-1}$, 7.0 *l* $N_2$ $min^{-1}$, 4.0 *l* air $min^{-1}$.



the flame; therefore the flame is hotter at the edges than it is at its center. Experiments showed[1,2,30] that $S_2$, HPO, and metal halide emissions are enhanced if the cavity is placed in the center of the flame, its cooler region (Salet phenomenon). Using a stainless steel cavity, Rix[40] studied the effect of cavity position in the flame on the conventional MECA temperature profile of a compound using a Thermodot optical pyrometer focused on the inner surface of the cavity. Figure 11 shows that a compound which vaporizes at 400°C will show a $t_m$ value of about 38s if the cavity is at the edge of the flame or 17s if the cavity is 4 mm inside the flame, thus exposing more of the cavity to the flame so that heat-up is faster.

### *c. Flame Composition*

The flame composition is important for MECA experiments; therefore optimization of gas flow rates should be carried out for each compound determined. The effect of flame composition on the cavity heat-up rate is shown in Figure 12.

Considering the dual role of the flame, i.e., to vaporize and to generate the emission, it is not surprising that many observations regarding the effect of flame composition on emission response vary with change in emitting species, cavity material, and analyte, and sometimes appear to be contradictory. For example, increasing the hydrogen flow rate in the flame has been shown to decrease $S_2$ emission[1,37,41] while increasing HPO emission.[15,41]

### *d. Solvent and Matrix Effects*

When conventional MECA is carried out on a solution, the solvent may greatly influence the response if the solvent evaporates during the time that the emission appears. It is well known that the presence of organic solvents suppresses $S_2$ emission in a hydrogen flame,[42] most probably by interacting with the hydrogen atoms required for producing the emitting species. Such an effect has been used as the basis of a gas chromatographic detector.[43] Veillon and Park[28] observed that the $S_2$ emission from an ethanolic solution of inorganic sulfur compounds was about 4 times less than that obtained from aqueous samples, and from a butyl acetate solution was 30 times less.

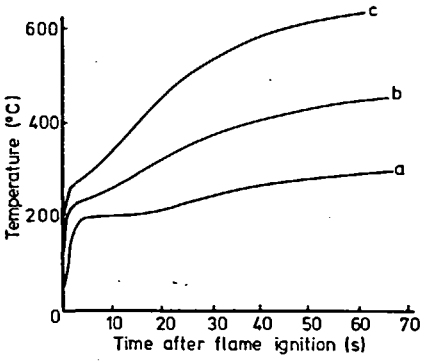



FIGURE 12. Increase in temperature of a stainless steel cavity introduced into the center of a flame having the following compositions:

| | $\ell$ min$^{-1}$ | | |
|---|---|---|---|
| | $H_2$ | $N_2$ | Air |
| (a) | 1.15 | 5.0 | 0.0 |
| (b) | 1.7 | 7.0 | 2.0 |
| (c) | 2.9 | 7.0 | 4.0 |

Everett et al.[44] found that the signal for 100 ppm of sulfur as sulfuric acid in 20% acetone had disappeared completely. Vaporized hydrocarbons containing sulfur gave $S_2$ intensities which decreased with the number of carbon atoms per molecule.[45]

Similar effects have been observed in MECA. Figure 13 shows the effect of allowing *n*-hexane to evaporate from its solution of promethazine in the cavity at room temperature.[12] Where no evaporation is allowed, hexane vaporization takes place at the same time as the disulfurization of promethazine, and $H_2S$ is evolved while the cavity space is rich in hydrocarbon vapors, with the resultant suppression of the emission. Some delayed breakdown seems to occur, however, because a small delayed peak ($t_m$ = 1.8 sec) appears. When the solvent is allowed to evaporate before inserting the cavity into the flame, an intense, sharp promethazine peak is obtained.

Organic solvents were also found to have a depressive effect on the response of organophosphorus compounds.[39] Figure 14 shows the variation of emission intensity and $t_m$ vs. solvent evaporation time from organophosphorus compounds in ethanol, benzene, and methyl isobutyl ketone, using stainless steel and aluminum cavities. The compounds with boiling points >200°C, e.g., tri-*n*-butylphosphine, triphenylphosphine oxide, and triphenylphosphate, have a constant emission intensity with increasing solvent evaporation time; the pure analyte remains in the cavity after the solvent has been evaporated. For compounds with lower boiling points, e.g., diethylphosphite and trimethylphosphate, a sharp decrease of the emission with increasing solvent evaporation time was noticed; the analyte evaporates concurrently with the solvent used. Figure 14 also indicates that when solvent is present, the HPO emission is delayed (larger $t_m$ values), but as more of the solvent is evaporated, the HPO response is faster. At maximal emission intensity, $t_m$ reaches a value which remains constant. The greatest sensitivity was generally achieved by using ethanol as solvent and an aluminum cavity.

There are several possible reasons for the quenching effect of the organic solvents on the formation and excitation of $S_2$ and HPO molecules. The hydrogen radicals which are normally involved in the chemiluminescence reactions are consumed in the

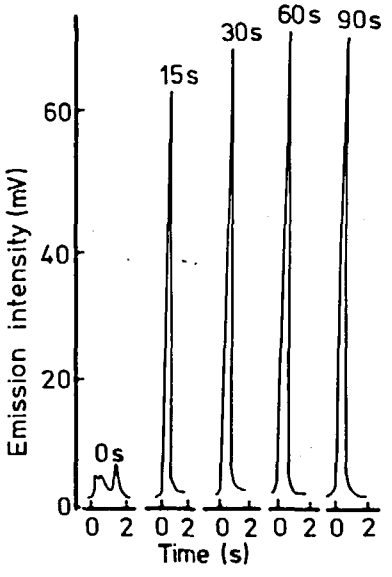



FIGURE 13. Effect of *n*-hexane evaporation time on the $S_2$ emission intensity from promethazine (10 ng of S in a 5-$\mu l$ sample) using a stainless steel cavity. Flame = 6.0 *l* $H_2$ $min^{-1}$, 6.0 *l* $N_2$ $min^{-1}$, 4.5 *l* air $min^{-1}$.



decomposition of the organic solvent. Further, removal of hydrogen atoms may occur by formation of hydrogen molecules promoted by carbon-containing molecules. The concurrent vaporization of analyte and solvent also leads to rapid production of solvent vapor in the cavity which decreases the residence time of the analyte vapor in the cavity, and hence the light emitted.

Water as a solvent can also influence MECA responses. The effect of evaporation of water from a promethazine solution[12] is shown in Figure 15. When water is present which would vaporize after 0 to 1 sec in the flame, the promethazine peak at 0.2 sec is greatly suppressed and a delayed ($t_m$ = 2.4 sec) peak appears. This is a similar situation to that of an organic solvent. As more of the water is evaporated before the cavity is introduced into the flame, the initial peak becomes more intense as does the second, which appears more and more quickly until it merges with the first peak. The effect of water could include removal of hydrogen atoms from the flame (see Equation 1) and diminishment of the catalyzed desulfurization of the heterocyclic ring.

Finally, a large amount of other compounds (inert or otherwise) can effect the MECA response merely by restricting access of the flame gases to the sample. For example, for the determination of sulfur in drug tablets,[37] coke,[15] and other solid materials,[46] the matrix ingredients decreased the emission intensity. Similar effects have been observed in carbon furnace atomic absorption spectrophotometry.[47]

### *e. Residue Formation in Cavity*

Another problem which can arise when samples contain relatively involatile components is the build-up of deposits, often of alkali metal salts, in the cavity. This can alter the reflective properties of the cavity surface, thus changing the emission intensity, and it can retard volatilization. Removal of such deposits, therefore, is essential. This is often difficult to achieve with stainless steel cavities without damaging the sur-

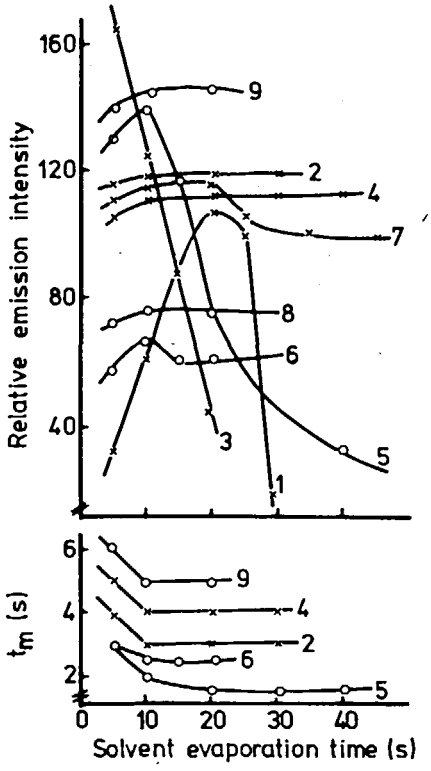



FIGURE 14. Effect of solvent evaporation: ethanol (a), benzene (b), and MIBK (c), from stainless steel (x), and aluminum (O) cavities; (1) trimethyl phosphate[c] (197.2°C); (2) tri-*n*-butyl-phosphine[a] (160°C); (3) diethylphosphite[a] (159°C); (4) tri-*n*-butyl-phosphine[c]; (5) triphenylphosphite[b] (360°C); (6) triphenylphosphine[b] (>360°C); (7) triphenylphosphine oxide[c] (>360°C); (8) triphenylphosphine oxide[b]; (9) triphenylphosphate[b] (245°C). (Boiling points in parenthesis.)

face. Carbon cavities are much more satisfactory in this respect. Another approach is to fit a silica liner to the cavity.[13] This is easily cleaned, and the steel surface below remains in its original condition.

The occurence of a high residue content in a sample is not uncommon. In such circumstances the advantages of employing conventional MECA are considerably diminished. The alternate procedure of MECA-VAP (see below) is not greatly affected by the refractory content of the sample, and again provides a useful alternative to the conventional approach.

### C. MECA Utilizing the Vaporization Reactor (MECA-VAP)

The functions of the cavity in MECA-VAP are reduced to its involvement in the generation of the emission (i.e., formation, excitation, emission of the emitting species) because the analyte is converted into a vapor in a closed reaction vessel. (For example, ammonium ions can be converted to ammonia by an alkali.[48] The vapor is transported to the cavity by a carrier gas, usually nitrogen. The cavity, which is in a fixed position

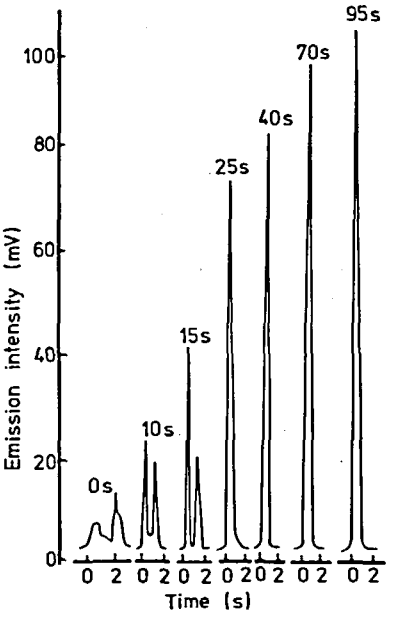



FIGURE 15. Effect of water evaporation time on the $S_2$ emission intensity from 15 ng of sulfur as promethazine in a 5-$\mu l$ sample using a stainless steel cavity.

in the flame in line with the detector, can simply be modified to provide an optional supply of $O_2$ to the cavity and/or an external supply of water for cooling.

In MECA-VAP, the same degree of speciation achieved by conventional MECA has only recently been reached[31] and this aspect is still being developed. This is compensated, however, by several attributes inherent in the method.

The techniques developed appear to be relatively interference free. Externally producing the analyte vapors permits optimization of the cavity conditions solely with regard to the generation of the emission. Selectivity is achieved by using selective reagents for the vaporization reactions. This is most useful, particularly for the separation of elements which emit in the oxy-cavity, which give broad, spectrally irresolvable emissions. Added selectivity and sensitivity can easily be accomplished by supplementing the technique with a chromatographic column or a cold-finger sample collector[49] between the vaporization vessel and the cavity detector. Details of the various applications are given below.

## III. EQUIPMENT

MECA can be carried out by simple modification of commercial flame emission spectrophotometers or atomic absorption spectrophotometers able to function in the emission mode.[2] The essential components of a MECA spectrophotometer are

**An emission burner unit** — This unit includes hydrogen, nitrogen, and air supplies.

**A monochromator** — Since most MECA emissions are bands, the monochromator need not be highly resolving. In fact, when lack of spectral overlap between the analyte emission and that of any other species can be accomplished, as is the case in various procedures, a simple optical filler will give greater sensi-

tivity by collecting a greater spectral range of the generated emission. However, the initial investigatory spectral measurements require the use of a good monochromator.

**A conventional photomultiplier detection system** — A great deal of amplification should be possible because of the very low background of the hydrogen flame (except around the OH peak at 306 nm).

**A read-out system** — Generally, this has been a fast response chart recorder (e.g., 0.2s for 90% f.s.d.) because MECA peaks may appear within 0.2 to 0.3s.

**A cavity-probe and holder** — Whereas the above components are readily available, the cavity-probe and holder are not (except as assembled in a complete apparatus — see below). However, they are easily constructed and can be arranged to fit into most commercial flame spectrophotometers. For a volatilization system, it is sufficient to assemble a device for permanently holding the cavity in the desired position in the flame. For the conventional system there must be a device for repeatedly introducing the cavity into the flame in the appropriate position and removing it when the measurement is complete, to enable the cavity to be cooled before introducing the next sample. Such devices have mainly involved rotation of the probe and its holder into a predetermined position in the flame (Figure 4), mainly because it allows injection of liquid samples with the probe in the vertical position. An alternative, however, is to have a permanently positioned cavity and a facility for turning the flame on and off as required without otherwise adjusting the flame gas flows.[11]

A complete MECA analyzer has been commercially available (MECA 22 Analyser, Anacon Inc., Houston, Tex.). This is now unavailable, but has been superseded by an improved instrument produced by Doma Instruments Ltd. It is also expected that a MECA sample holder device suitable for attachment to available flame spectrometers will soon be commercially available.

In the remainder of this paper, the applications of MECA in its various adaptations to a wide variety of compounds are described. They are dealt with element by element, and emphasize the sensitivity, selectivity, and variety of MECA determinations, as well as numerous modifications that can be invoked for specific purposes and the continuing importance of chemical reactions in the MECA processes.

## IV. APPLICATIONS OF CONVENTIONAL MECA

### A. Applications to Solutions

#### *1. Sulfur Compounds*

Inorganic and organic sulfur compounds give the characteristic blue $S_2$ emission in the MECA cavity in a nitrogen-diluted hydrogen flame. The multipeaked band emission has its most intense peaks between 350 and 410 nm (Figure 3), although the emission can be detected at wavelengths as long as 520 nm. Addition of a little air to the flame almost completely destroys the $S_2$ emission, but more air restores the emission.[2,11,37]

All sulfur anions give an emission, the $t_m$ values increasing with their increasing involatility and stability (Table 1). The $t_m$ values are also influenced by the cation(s) present with the anion. Thus, especially for sulfate, sulfuric acid emits much earlier than copper sulfate, which in turn emits much earlier than sodium sulfate. Because of this, the sulfates with larger $t_m$ values give less intense emissions because the cavity surface is hotter, thus reducing any Salet phenomenon enhancement (p.000), and because the rate of temperature increase is lower, thus making the peaks broader. The magnitude of the response from sulfate, therefore, depends on the cations accompa-

Table 1
MECA CHARACTERISTICS OF SOME INORGANIC SULFUR COMPOUNDS IN A STAINLESS STEEL CAVITY WITH SILICA LINER

| Compound | $t_m$[a] (sec) | Detection limit (ng S/5 μl) | Slope of log-log plot |
|---|---|---|---|
| $Na_2S$ | 2.0 | 5[b] | 1.4 |
| KSCN | 18.0 | 5[b] | 2.0 |
| $Na_2SO_3$ | 2.4 | 6[c] | 1.9 |
| $Na_2S_2O_3$ | 2.0; 10.0 | 10[d] | 1.7 |
| $Na_2SO_4$ | 40.0 | 20[c] | 1.8 |
| $Na_2S_2O_8$ | 40.0 | 20[d] | 1.6 |
| S[e] | 1.5 | 0.4 | 1.2 |
| $Na_2S_2O_4$[e] | 7.5 | 5[b] | 1.1 |
| $Na_2S_2O_6$[e] | 11; 20 | 1.5, 5[c] | 2.1, 0.8 |

[a] Flame: 1.7 l $H_2$ $min^{-1}$, 4.0 l $N_2$ $min^{-1}$.
[b] $0.6 \times 10^{-2}$ $M(NH_4)_2HPO_4$.
[c] 0.1 $M H_3PO_4$.
[d] $2 \times 10^{-2}$ $M$ phosphate buffer.
[e] Without silica liner.

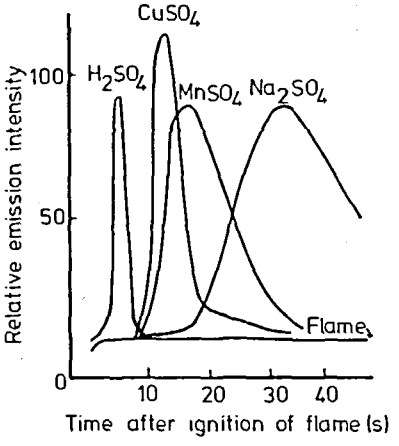



FIGURE 16. MECA responses for various sulfates (arbitrary amounts). Flame = 6.0 l $H_2$ $min^{-1}$, 6.0 l $N_2$ $min^{-1}$, 4.5 l air $min^{-1}$.

nying it. Figure 16 shows the $S_2$ response from the sulfates of copper, manganese, and sodium.[1] Such responses would be useless for the determination of sulfate when metal ions were present because overlapping responses would be obtained, generally of the most refractory sulfates.

Addition of phosphoric acid to an aqueous metal sulfate solution increases the intensity of the emission and makes it appear earlier. Figure 17 shows the effect of adding different amounts of phosphoric acid to a solution of iron(II) sulfate. The $t_m$ decreases until at a phosphoric acid concentration of 0.072 $M$, the response is the same as that of sulfuric acid under the same acid conditions. The phosphate ions form the more

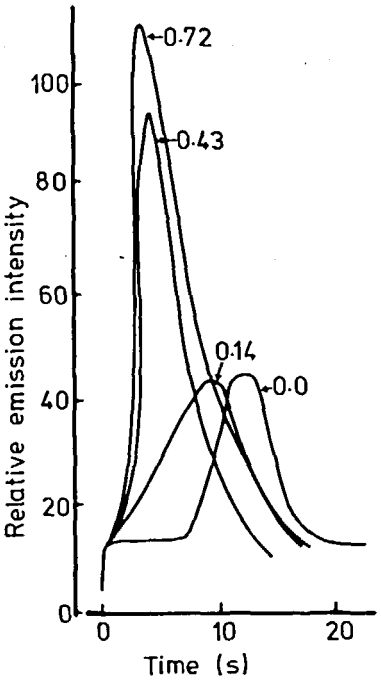



FIGURE 17. Effect of phosphoric acid on the iron(II) sulfate emission (the numbers are molar concentrations of phosphoric acid).



stable iron phosphate, thereby replacing the sulfate, which then responds as sulfuric acid. Other acids (e.g., hydrochloric, hydrofluoric, nitric) have no effect on the emission from metal sulfates, while perchloric acid has a depressive effect in most cases.[13]

Other sulfur anions are affected in this way by cations, but to a much lesser extent. The effect can again be removed by adding phosphoric acid or, in the case of sulfide and thiousulfate, because of loss of hydrogen sulfide from their acidic solutions, by adding diammonium hydrogen phosphate.[13]

Under these conditions, sensitive determinations of any one of the sulfur anions can be achieved (Table 1). As can be seen, the detection limits for the anions with small $t_m$ values are markedly greater than those with larger $t_m$ values. The calibration graphs all have a sigmoid shape, as is usually found in similar systems not involving a MECA cavity.[50] The curved lower part of the curve is to be expected because of the kinetics of the formation of $S_2$ emitters. A log-log plot of this region of the graph gives a straight line, the slope of which should be 2.0 if the rate-determining step for the formation of the emitting species is entirely the combination of two sulfur species to form $S_2$*.[51] In practice, the slope often approaches 2 (Table 1), but sometimes can be significantly less. The upper curvature of the graph has been suggested as resulting from a limitation of intensity by self-absorption.[52] An attempt to "correct" such a curve on this basis was unsuccessful.[53] A more likely explanation is the formation of more highly polymerized vapor phase sulfur species at the higher concentrations. In the MECA cavity, such species ($S_4$, $S_8$, etc.) would be expected to condense on the cavity walls. Such deposits have been shown to be formed by repeating MECA experiments in the same uncleaned cavity, without adding more sample.

A further explanation for limited $S_2$ intensity, which is particularly relevant to MECA but might also apply in aspiration or entirely gas-phase systems, is the change

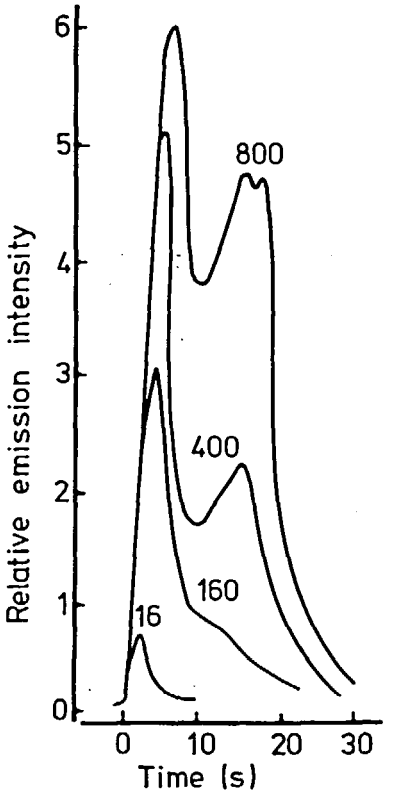



FIGURE 18. Emission profiles for increasing amounts of thiourea (numbers are nanograms of sulfur as thiourea). (From Belcher, R., Bogdanski, S. L., and Townshend, A., *Anal. Chim. Acta*, 67, 1 (1973). With permission.)

in the decomposition reaction sequence when large amounts of material are present in the cavity. This results in the production of one or more later MECA peaks in addition to the original fastest peak. As the amount of sulfur compound in the cavity increases, the $t_m$ of the initial, single peak increases slightly, but further peaks also appear. This is illustrated in Figure 18 for thiourea. The effect arises from interaction of some of the initial decomposition products with undecomposed sample, to a form a less volatile product and, probably, the deposition of sulfur.

In the particular case of sulfur compounds, such a multi-peaked response cannot be accommodated by an integration procedure without great difficulty, mainly because the intensity of emission is dependent on the cavity wall temperature (Salet phenomenon), and thus the specific intensity (per unit mass of sulfur) is continually decreasing as the temperature is raised. Also, the dependence of the intensity on the square (or some fractional power) of the mass of sulfur is a complicating factor. For analytical reliability, therefore, it is recommended that the amount of sample in the cavity should not be sufficient to produce more than a single-peaked response for a given compound.

Such MECA responses are readily applied to the determination of traces of sulfur anions. Particular attention has been given to sulphate determination because of the lack of sensitive methods for this anion. Using phosphoric acid to mask interfering cations, ppm levels of sulfate have been determined in natural and high purity waters,[54] wines, dusts, and soils,[55] without tedious pretreatment.

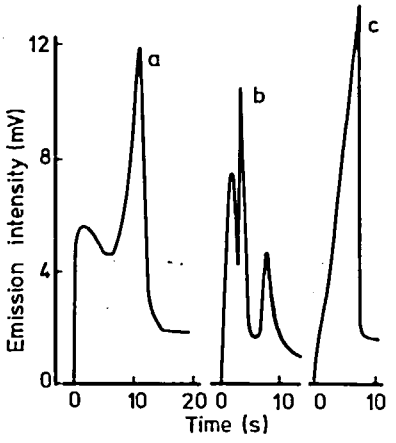



FIGURE 19. MECA responses in a stainless steel Allen screw from 5 $\mu l$ of 20 ppm S as sodium thiosulfate in the presence of $2.8 \times 10^{-2}$ *M* phosphate buffer. (a) $H_2$ = 3.2 *l* $min^{-1}$, $N_2$ = 7.0 *l* $min^{-1}$; (b) $H_2$ = 3.2 *l* $min^{-1}$, $N_2$ = 7.0 *l* $min^{-1}$, air = 4.0 *l* $min^{-1}$; (c) 12 ppm S as potassium thiocyanate: flame composition as (a). (From Al-Abachi, M. Q., Belcher, R., Bogdanski, S. L., and Townshend, A., *Anal. Chim. Acta*, 86, 139 (1976). With permission.)



A particularly elegant application is the determination of sulfate in urine.[56] Dilution of a small sample of urine 100 times with 0.1 *M* phosphoric acid, and injection of 5 $\mu l$ into a carbon cavity in a $H_2$-$N_2$-air flame gives a sharp sulfate peak, which gives a rapid and direct measure of the sulfate concentration.

The $t_m$ values for the common sulfur anions and elemental sulfur vary over a tenfold time span (Table 1). For this reason, it is possible to obtain resolved peaks from nearly all binary and a number of ternary mixtures (see Figure 9) of such anions by selection of appropriate flame conditions. This allows rapid analysis of such mixtures by a single experiment.

Resolution of a four-component sulfur-anion mixture in this way has so far proved impossible. However, chemical separation before MECA can be applied to enable a four-component mixture to be analyzed.[55]

A number of sulfur anions give multipeaked responses, which can be attributed to their mode of breakdown. Thiosulfate, for example, gives two peaks of $t_m$ = 2 sec and 10 sec, in the presence of phosphate buffer, when a hydrogen-nitrogen flame (3.2 l $min^{-1}$, $N_2$ = 7.0 l $min^{-1}$) is used (Figure 19a). If air is introduced into the flame, a three-peak sequence appears (Figure 19b). The three peaks may arise because the decomposition[14] of sodium thiosulfate follows the reaction sequence:

$$4Na_2S_2O_3 \cdot 5H_2O \rightarrow 4Na_2S_2O_3(\ell) + 5H_2O(g) \quad (14)$$

$$4Na_2S_2O_3(\ell) \rightarrow 3Na_2SO_4(s) + Na_2S_5(s) \quad (15)$$

$$Na_2S_5(s) \rightarrow Na_2S(s) + 4S(\ell) \quad (16)$$

The three peaks would correspond (in order of increasing $t_m$) to sulfide, sulfur, and sulfate. In a cooler flame, a different breakdown mechanism occurs:

$$Na_2S_2O_3(\ell) \rightarrow Na_2SO_3(s) + S(s) \quad (17)$$

Therefore, the two peaks (Figure 19a) would correspond (in order of increasing $t_m$) to sulfur and sulfite.

Thiocyanate gave a nonsymmetrical peak in the presence of phosphoric acid (Figure 19c). The reason is not clear, but may result from depolymerization of the thiocyanic acid formed on addition of the acid.[55]

Dithionite gives at least four peaks, three of which can be identified as sulfur or sulfide, sulfite, and sulfate, in agreement with its suggested decomposition:[6]

$$2S_2O_4^{2-} \rightarrow S_2O_3^{2-} + SO_3^{2-} + SO_2(g) \quad (18)$$

$$S_2O_3^{2-} \rightarrow SO_4^{2-} + S^{2-} \quad (19)$$

Dithionate gives just two peaks, the one with the larger $t_m$ corresponding to sulfate, the other corresponding to its breakdown to sulfur dioxide:[6]

$$S_2O_3^{2-} \rightarrow SO_2(g) + SO_4^{2-} \quad (20)$$



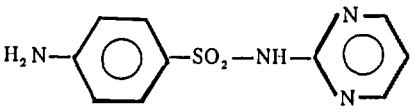
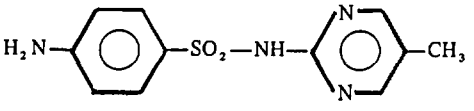
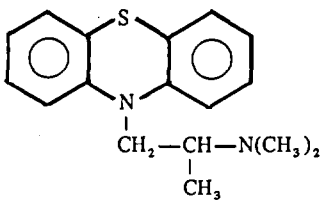
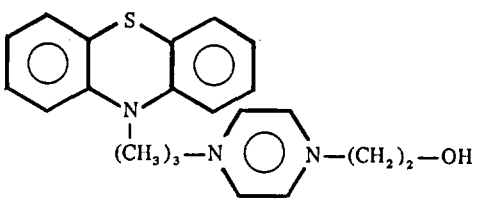
Organic sulfur compounds give MECA $S_2$ emissions, often with sufficient sensitivity to detect sub-ng amounts. For example, the detection limits for thiourea and diphenyl sulfide are 25 pg and 30 pg of S, respectively. As with inorganic compounds, the sensitivity decreases as the $t_m$ value increases, so that the less volatile or less easily decomposed compounds give appreciably less intense emissions than those which emit very rapidly. This behavior is demonstrated very clearly with certain sulfur-containing drugs,[12,37] as discussed below.

A study of a number of sulfonamide and triazine drugs has not only provided a very sensitive means of determination of these compounds, but has thrown some further light on the effect of structure on MECA behavior. Some characteristics of their MECA behavior[12,37] are given in Table 2. All the simple sulfonamide and related compounds give a single peak response with a $t_m$ of approximately 2 sec, a detection limit of approximately 2 ng of sulfur, a linear calibration graph with a slope, therefore, for the log-log calibration graph of $\simeq 1$. The relatively low sensitivity achieved for these types of compounds is probably a consequence of the strong bond formed between sulfur and oxygen ($S = O \simeq 119$ Kcal $mol^{-1}$). A similar decrease in sensitivity is noted for sulfite with respect to sulfide.[13] The mild hydrogen flame will be less effective in breaking such bonds compared to the much weaker S–C bond ($\simeq 65$ Kcal $mol^{-1}$).

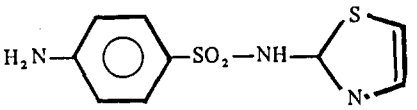
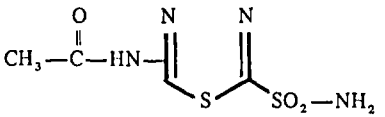
The three triazines also gave single-peaked responses of $t_m = 0.2$ sec, with nonlinear calibration graphs, a detection limit of approximately 0.3 ng of sulfur, and much greater sensitivity, as would be expected at the lower cavity temperature. The compounds containing two sulfur atoms in the molecules (Table 2) also exhibit linear calibration graphs if the first peak (triazole sulfur) is measured. The limit of detection and sensitivity resemble the values for triazines. Some calibration graphs are shown in Figure 20. All the triazines are derivatives of thiodiphenylamine, reported to decompose at 371°C.[57] However, at 0.2 sec, the stainless steel cavity is just over 100°C; this quick vaporization is probably catalyzed by the steel cavity surface (as described earlier) in the presence of hydrogen radicals from the flame.

The substitution of a steel cavity by carbon had only a little effect on the $t_m$ values of the sulphur drugs, but it markedly decreased (by $\geq 5$ times) the sensitivity for all the drugs tested. The change of cavity material also changed the behavior of the drugs in the flame. For example, promethazine gave a fast emission ($t_m = 0.2$ sec) in the

## Table 2
## MECA BEHAVIOR OF SOME SULFUR-CONTAINING DRUGS

| Drug | Structure | $t_m$ (sec) | Linear calibration range (ng S) | Detection limit (ng S/5 $\mu l$) |
|---|---|---|---|---|
| Sulfadiazine |  | 2.0 | 15—120 | 2.0 |
| Sulfamerazine |  | 2.1 | 15—150 | 2.0 |
| Promethazine |  | 0.2 | 0.4—4.0 | 0.2 |
| Perphenazine |  | 0.2 | 0.5—4.0 | 0.3 |

## Table 2 (continued)
## MECA BEHAVIOR OF SOME SULFUR-CONTAINING DRUGS

| Drug | Structure | $t_m$ (sec) | Linear calibration range (ng S) | Detection limit (ng S/5 μl) | |
|---|---|---|---|---|---|
| Sulfathiazole |  | | 0.3<br>(1.2)[a]<br>2.1 | 2—12 | 0.7 |
| Acetazolamide |  | | 0.9<br>1.2 | 10—50 | 1.5 |

[a] Shoulder.

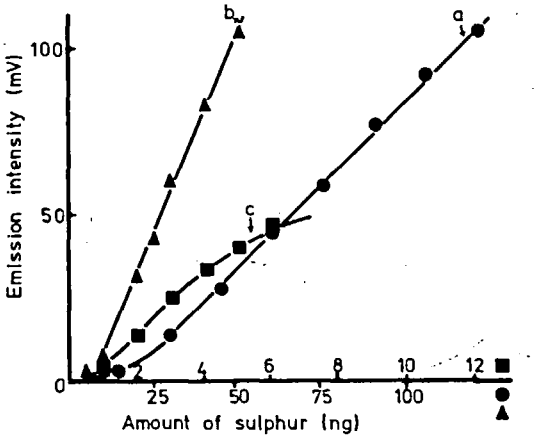



FIGURE 20. Calibration graphs after solvent evaporation for (a) sulfadiazine, (b) acetazolamide (measuring the first peak), (c) perphenazine.

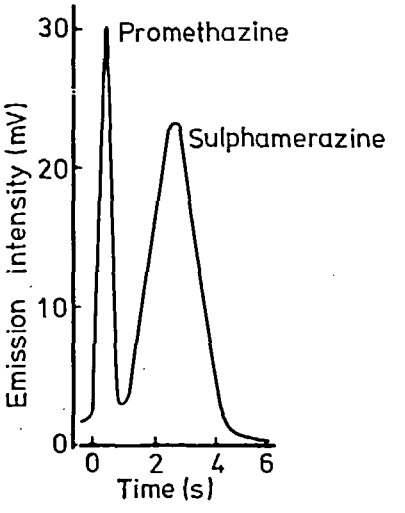



FIGURE 21. Resolution of a mixture of promethazine hydrochloride (3 ng S) and sulfamerazine (40 ng S) using a stainless steel cavity, after acetone evaporation.

steel cavity, whereas in the carbon cavity, two peaks of $t_m$ = 0.2 and 1.5 sec at least 33 times less sensitive than in the steel cavity were obtained.

A mixture of promethazine and sulfamerazine gave resolved MECA peaks in a steel cavity (Figure 21). The triazine had no effect on the peak height of the sulfonamide, but increasing amounts of the sulfamerazine (>40 ng of S) gradually suppressed the emission of the triazine, presumably by interfering with its decomposition reaction.

Two of the drugs tested, sulfathiazole and acetazolamide, contained a heterocyclic and a sulfonamide sulfur atom (Table 2). Both of these compounds gave a double-peaked response, even near the detection limit. The earlier peak ($t_m$ = 0.3 sec for Sulpathiazole and 0.9 sec for acetazolamide) possibly signified removal of sulfur from

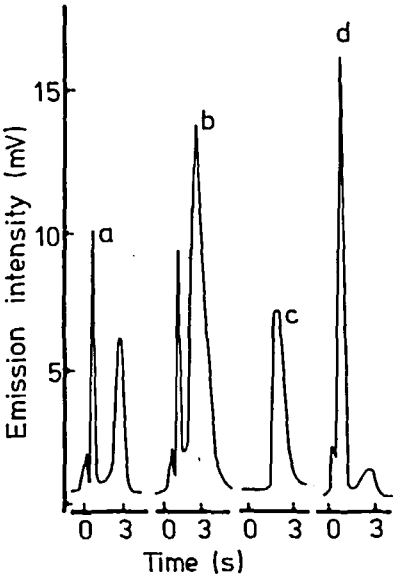



FIGURE 22. MECA response in a carbon cavity from 5 $\mu l$ of a solution of (a) 500 ppm serum albumin, (b) 500 ppm serum albumin + few crystals of ammonium sulfate, (c) dilute solution of ammonium sulfate, (d) 1000 ppm egg albumin.



the ring; the later peak ($t_m$ = 2.1 and 1.2 sec, respectively) signified removal of the sulfonamide group.

Analytical procedures were devised as a result of these experiments. For determinations of sulfur drugs in tablets, matrix ingredients (starch, lactose, magnesium stearate, dye) should be removed. Otherwise, they would depress the emission of the drug, mainly because of the masking effect of their bulk. This was done by grinding up the tablet and extracting the drug with acetone. For the heterocyclic drugs, this was achieved by grinding up the tablet, dissolving it in water, making the pH 11 with 2 *M* sodium hydroxide and extracting the drug into *n*-hexane. A similar extraction procedure was used for injection solutions to separate the drug from sodium sulfite added as stabilizer.

Many other organic sulfur compounds give characteristic MECA $S_2$ responses. These include vitamins (triamine ($B_1$) and biotin [H]), amino acids (methionine, cysteine, cystine, taurine, penicillinamine, and glutathione) and proteins, which give peaks very similar to the individual amino acids.[12] Saccharin has been successfully determined in fruit juices after a simple ether extraction.[58]

An interesting MECA application is the distinction between sulfur-containing protein and inorganic sulfate in egg albumin and serum albumin preparations. Injection into a carbon cavity of 5-$\mu l$ aliquots of solutions containing 1000 ppm of egg albumin and serum albumin showed three peaks with $t_m$ = 0.2 sec, 0.8 sec (protein), and 2.4 sec (sulfate). (See Figure 22).[12]

MECA has also been useful for the determination of sulfates and sulfonates in detergents.[59] Organic sulfonates ($RSO_3^-$) gave multipeaked responses. Sodium dodecylbenzene sulfonate gave two peaks; the first was quite rapid ($t_m$ = 2 sec), followed by a second, broad, delayed peak ($t_m$ = 36 sec), very similar to that given by sodium sulfate. Addition of phosphoric acid speeded up the response and gave an unresolved

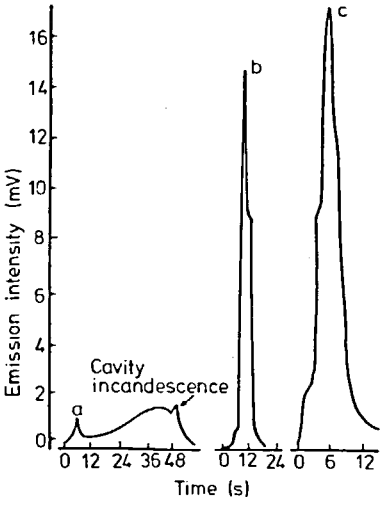



FIGURE 23. MECA response of (a) sodium dodecylbenzene sulfonate (35 ppm S) alone, (b) in the presence of 0.1 *M* $H_3PO_4$, (c) sodium hexadecene sulfonate (100 ppm S) in 0.1 *M* $H_3PO_4$ (carbon cavity).



three-peaked response, the last peak having the same $t_m$ value as sodium sulfate in 0.1 *M* phosphoric acid (Figure 23). The use of a stainless steel cavity gave irreproducible results, probably because of carbon deposition which blackened the cavity surface. A carbon cavity was satisfactory. Measurement of the second, most intense peak allowed the determination of $\geq$ 2 ng S $\mu l^{-1}$ as dodecylbenzene sulfonate in a 5-$\mu l$ injection. The detection limit is 2.5 ng of S.

Sodium hexadecene sulfonate and *p*-xylene-2-sulfonic acid in 0.1 *M* phosphoric acid behaved in a similar way, although the latter gave only two peaks. Other sulfonates not used in detergents (naphthalene-2-sulfonic acid, camphor-*D*-sulfonic acid and *p*-toluene sulfonic acid) also gave double peaks in phosphoric acid, at the 100 ppm S level. The sensitivities were generally similar. However, the most intense response peak for sodium hexadecene sulfonate was the third. As this appeared later than the most sensitive second peak for sodium dodecylbenzene sulfonate, the sensitivity for the hexadecene sulfonate was less than that for the dodecylbenzene sulfonate (Figure 23).

Organic sulfates ($ROSO_3^-$) such as sodium lauryl sulfate gave only a weak, delayed response, similar to inorganic sulfates. As with the latter, however, the response was much faster and more intense in the presence of 0.1 *M* phosphoric acid, having the same $t_m$ value as sodium sulfate and the third peak of sodium dodecylbenzene sulfonate, under the same conditions.

It is likely that the phosphoric acid hydrolyzes the organic sulfate on heating in the cavity[60] with release of sulfuric acid, thus accounting for the similar responses of inorganic and organic sulfates, and the fact that mixtures of the compounds give responses of equal magnitude in a carbon cavity. The detection limit is 10 ng of sulfur.

Commercial detergents may have inorganic and organic sulfates and a sulfonate present. A sulfonate response can be resolved from the other two, but all three compounds give a response at the sulfate peak, thus making measurement of the individual sulfate components difficult. Although this problem is probably soluble, at present a separation procedure has been devised for measuring the three components based on

a *p*-toluidine extraction into carbon tetrachloride.[61] In one stage, organic sulfate and sulfonate were extracted, leaving only sulfate ions in the aqueous solution, which could be determined directly. Curiously, the sensitivity for the sulfonate in the extract was very poor; thus the extract could not be used for further analysis. In a second experiment, the test solution was boiled for 25 min with phosphoric acid. This hydrolyzes the organic sulfate so that extracting with *p*-toluidine removes just the sulfonate, and the total sulfate was determined in the aqueous layer. Finally, the total sulfur content of the detergent was measured after oxygen flask combustion. Note that the phosphorus content of detergents is also readily measured by MECA (see below). The lack of sensitivity for sulfonate extracted as an ion-pair with *p*-toluidine prevented the desired application of this technique for measuring traces of such detergent components in river water, etc. However, the ion-pair extraction with methylene blue[62] gave a sensitive MECA emission after evaporation of the solvent in the cavity, could be used to concentrate sulfonates for MECA measurement.

### 2. *Indirect Measurements Based on $S_2$ Emission*

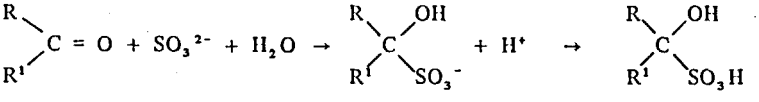
It is possible to greatly extend the applications of MECA by converting the analyte into sulfur-containing compounds and then measuring their $S_2$ emission. Amines and amino acids, for example, can be converted to their dithiocarbamates by reaction with carbon disulfide.[36] Amines react sufficiently rapidly for the reactants to be mixed directly in the cavity. After about 1 min, the excess of carbon disulfide has evaporated leaving the dithiocarbamate formed as the only sulfur-containing species. Generally, amines in the microgram range could be determined. Amino acids reacted too slowly for *in situ* conversion; dithiocarbamate formation was achieved by a 3-hr reaction in a graduated flask. Because such a process eliminates any possibility of loss of reagent during the reaction, the extent of reaction in such a procedure is much greater than in the *in situ* situation and much greater sensitivity is achieved, the linear calibration ranges being typically ten times more sensitive for the amino acids. No doubt a similar sensitivity would be achieved for amines under such conditions. No separation of compounds could be achieved by this procedure.



When acetone was used as a solvent for *in situ* reactions, a high blank response, attributed to various sulfur impurities in carbon disulfide, was obtained. Comparison of $t_m$ values under the same conditions proved that sulfite, present as an impurity in carbon disulfide, formed a less volatile compound which remains in the cavity after the evaporation of carbon disulfide, and thus was partly responsible for the flame response. A reduction of 50% of the blank response occurred when *n*-hexane was used as a solvent instead of acetone, and a further 90% reduction was observed when Analar carbon disulfide was used, Thus, the procedure could be used for the isolation of sulfur-containing impurities in various reagents and subsequent measurement via $S_2$ emission.

*In situ* analysis has also been applied to the determination of some metal ions. For example, an acidic aqueous copper(II) solution was injected into a silica-lined stainless steel cavity,[40] with subsequent addition of a few drops of hydrogen sulfide in acetone. Excess of reagent and solvent were evaporated off in an oven, and the MECA response from the metal sulfide residue was measured.

The indirect determination of carbonyl compounds is also possible[63] based on the formation of sulfite addition compounds:




(21)

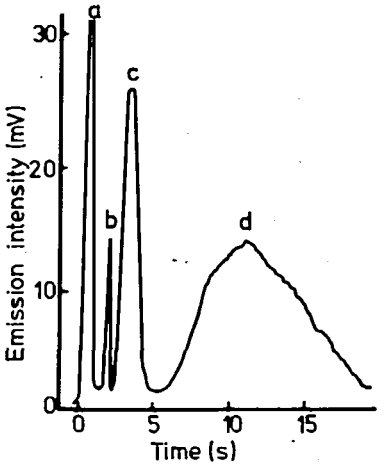



FIGURE 24. MECA response from a 5-$\mu l$ solution originally containing 120 ppm of 2-amino-2-methyl-1-propanol, $2.4 \times 10^{-3}$ $M$ $NaIO_4$, $12 \times 10^{-3}$ $M$ $Na_2SO_3$, and 0.06 $M$ $H_3PO_4$. (a) Excess sulfite, (b) acetone-sulfite addition compound, (c) formaldehyde-sulfite addition compound, (d) sulfate.



If an excess of sodium sulfite is added to the carbonyl compound, followed by phosphoric acid, the MECA response, when reaction is complete, comprises two peaks. The first peak is the unreacted sulfite, but the second is that the sulfite addition compound, release of sulfur dioxide vapor being retarded by compound formation. Formaldehye (2 to 750 $\mu g$), acetaldehyde (0.05 to 1.0 mg), and acetone (0.4 to 3.5 mg), for example, can be determined in this way. Also, since acetone binds sulfite less strongly than formaldehyde, a mixture of both compounds gives resolved sulfite addition compound peaks, enabling both compounds to be determined. Some aromatic aldehydes, such as benzaldehyde, *p*-dimethylaminobenzaldehyde, *p*-chloraminobenzaldehyde, and *p*-nitroaminobenzaldehyde were also determined, with detection limits between 1.0 and 1.7 ng in 5 $\mu l$ of solution injected.[55]

This principle has been extended to the determination of microgram amounts of carbonyl compounds produced by periodate oxidation[64] of *vic*-diols,[63] $\alpha$-amino alcohols,[63] and other polyhydroxy compounds,[55] e.g.,

$$(CH_2OH)_2 \cdot (CHOH)_4 + 5IO_4^- \rightarrow 2HCHO + 4HCOOH + 5IO_3^- + H_2O \qquad (22)$$

The carbonyl compound produced reacts with sulfite to form the addition complex. In each instance, the free and bound sulfite peaks are joined by a third later peak caused by sulphate formed by oxidation of sulfite by periodate and/or iodate. During this reaction, some compounds, e.g., 2-amino-2-methyl-1-propanol or 1-phenyl-1,2-ethanediol, produce acetone and formaldehyde or benzaldehyde and formaldehyde, respectively. Addition of sulfite then gives rise to four peaks,[55] as indicated in Figure 24.

Finally, a procedure based on the catalyzed oxidation of ethanol to acetaldehyde was developed.[9] Yeast alcohol dehydrogenase was used as a catalyst. The ethanol, in

the presence of the enzyme at pH 8, was oxidized to acetaldehyde in about 10 min at 25°C. The acetaldehyde produced, when treated with sodium sulfite (0.05 *M*), formed a sulfite addition compound which was monitored by MECA. The minimum amount of ethanol detected by this technique was 10 ng. Other alcohols tested, e.g., methanol, *n*-propanol, and isopropanol, gave rise to very weak emissions.

Based on the same procedure, some heavy metals which inhibited the oxidation of the alcohol were indirectly determined.[9] Mercury(II) and silver were so determined in the range 0.05 to 0.175 ng/5 $\mu\ell$, respectively.

Because of the low temperature of the hydrogen-nitrogen flame employed in MECA, most metals do not give any emission when their salts are injected directly into the cavity. An indirect means of determining some metals is via $S_2$ emission given by a thiilogand forming a chelate with the metal. An example is the determination of nanogram amounts of cobalt by measuring the emission given by its volatile chelate formed with monothioacetyl acetone. A few microliters of the chelate dissolved in *n*-hexane were injected into an aluminum water-cooled cavity, the solvent evaporated, and the $S_2$ emission from the residue measured. The detection limit was 0.3 ng of cobalt. Nickel, cadmium, and lead can also be determined in the same way, but the sensitivity was poorer since their chelates were not as volatile as the cobalt chelate. Furthermore, the chelate was accompanied by unreacted ligands, which constituted a serious interference.

The use of diethyldithiocarbamate to form extractable manganese, iron, cobalt, nickel, copper, lead, cadmium, and mercury chelates solved the problem of excess ligand since the ligand is stable in water and is not extracted with the chelate at pH > 8. This technique[40] allows the determination of sub-ng amounts of the metals and could be further improved by changing the conditions of extraction. Using selective extraction procedures to precede the dithiocarbamate extraction, no serious interferences were noticed, except of copper in the determination of nickel. For example, the procedure followed for manganese determination involved a dithizone extraction of pH 6.5 to 7.0 followed by a back extraction with hydrochloric acid. To the aqueous solution, after adjusting the pH to 9.0 with ammonia, sodium diethylthiocarbamate was added and the resulting manganese dithiocarbamate was extracted with carbon tetrachloride. Manganese was then determined in the organic layer. Similarly, 10 to 25 ng of palladium was determined by measuring the $S_2$ emission from its monothiotrifluoroacetyl acetone chelate.[65]

### *3. Phosphorus Compounds*

Determination of phosphorus by MECA in inorganic and organic compounds is based on the green HPO emission which appears in the cavity. The spectrum shows three main bands at 513, 528, and 563 nm, with that a 528 nm normally used for quantitative work.[1]

When an aqueous solution of orthophosphoric acid is injected into the MECA cavity, a sharp peak is recorded just after the cavity is introduced into a $H_2/N_2$ flame. It was observed that the responses from large amounts of phosphoric acid (>200 $\mu$g) were broader and more flattened at the maximum intensity than those from smaller amounts. The $t_m$ values slightly increased with increasing amounts injected. Introduction of air into the flame was found to intensify the emission. In a relatively hot flame (5.3 $\ell$ $H_2$ $min^{-1}$, 4.2 $\ell$ $N_2$ $min^{-1}$, and 5.4 $\ell$ air $min^{-1}$) orthophosphoric acid gave a single peak response. Repeating the experiment with a cooler flame (3.4 $\ell$ $H_2$ $min^{-1}$, 5.5 $\ell$ $N_2$ $min^{-1}$, and 2.5 $\ell$ air $min^{-1}$) produced a double peaked response (Figure 25). This behavior could be attributed to the possible formation of reaction products which vaporize at different cavity temperatures.[15] For example, it is known that on heating orthophosphoric acid solution dehydrates and yields pyrophosphoric acid:

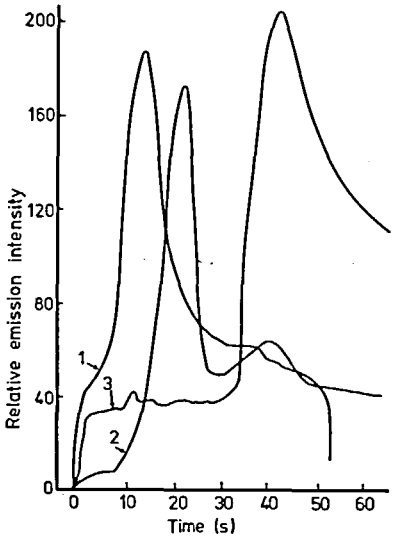



FIGURE 25. MECA HPO responses from orthophosphoric acid showing (1) one peak ($H_2/N_2$/air = 5.3/5.5/5.4 *l* $min^{-1}$), (2) two peaks ($H_2/N_2$/air = 3.4/5.5/2.5 *l* $min^{-1}$), (3) one peak after preheating the sample for 40 sec before introducing air into the flame.

$$2H_3PO_4 \xrightarrow[-H_2O]{} H_4P_2O_7 \qquad (23)$$

It was assumed, therefore, that the two peaks appeared as a result of the sequential vaporization of the two acids. Preheating the orthophosphoric acid in the cavity with a mild hydrogen diffusion flame for 40 sec so that no emission was observed and then introducing air into the flame gave only the second peak, showing that the orthophosphoric acid had probably been converted to pyrophosphoric acid. To prevent the appearance of two peaks, the hotter flame is recommended.[15]

Alkali and alkaline-earth metals greatly suppress the emission[1,15,66] because of the formation of refractory metal phosphates. Perchlorate and borate also decrease the HPO emission, probably by altering the radical population within the cavity. Perchloric acid, for example, decomposes on heating with release of oxygen, which is detrimental to the formation of HPO with the cavity. Sulfate, however, appears to increase the HPO emission; addition of excess of sulfate resulted in the emission at 528 nm having two peaks, with $t_m$ values corresponding to sulfuric and perchloric acids, respectively. The sulfuric acid emission, however, was from $S_2$, showing that $S_2$ can be measured at 528 nm.

Other inorganic phosphorus salts such as phosphites, hypophosphites, and polyphosphates gave very faint HPO emissions, probably because of the inability of the MECA flame to vaporize such refractory salts.[15,66] Although perchloric acid reduced the HPO emission from phosphoric acid, dissolution of the above phosphorus salts in 0.6 *M* perchloric acid significantly increased their HPO emission (Figure 26). The data in Table 3 show that the $t_m$ values for all phosphorus salts investigated were the same as for phosphoric acid in the presence of perchloric acid. Perchloric acid, however, does not effectively remove all cation interference effects. The addition of sulfuric acid

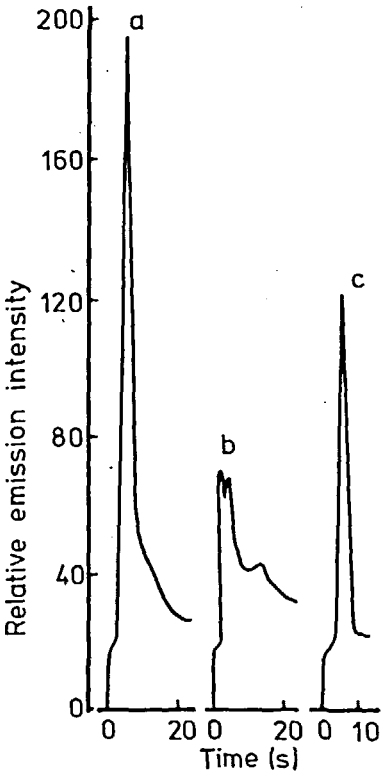



FIGURE 26. MECA HPO emission responses from phosphoric acid (70 ppm). (a) Alone, (b) with 0.6 *M* perchloric acid, (c) sodium tripolyphosphate (50 ppm) with 0.6 *M* perchloric acid.



to inorganic solutions was found to be more effective in this respect. It also gives slightly greater intensities than perchloric acid (Table 3).

All phosphorus(V) anions, independent of the cation present, have the same $t_m$ and a similar emission intensity per nanogram of phosphorus in the presence of sulfuric acid. Thus it is likely that the acid converts them to orthophosphoric acid, which vaporizes in the cavity.

The calibration graph is linear up to 100 $\mu g/5\ \mu l$ of phosphorus (by peak height). The detection limit achieved is 0.5 ng of phosphorus.

The fact that nanogram amounts of phosphorus as any of its anions can rapidly be determined with the same sensitivity by simply adding 0.3 *M* sulfuric acid makes the technique very attractive for applications to total phosphorus determinations in real samples. Examples are the determination of phosphorus in rocks[67] and detergent powders.[59,66] The rock samples were fused with sodium carbonate and the residue dissolved in gently heated hydrochloric acid (1 + 4). The siliceous residue formed was filtered off and phosphorus was determined in the aqueous solution after addition of sulfuric acid to prevent cationic interferences. The method has the advantage of speed and freedom from most interferences encountered in spectrophotometric methods.

Triphosphates are added to improve the performance of a washing powder, so an accurate determination of phosphorus in detergent powders is essential. For MECA purposes, the sample must first be ashed to eliminate the depressive effect of the organic components. The results compared favorably with those obtained by the quino-

Table 3
EFFECT OF THE PRESENCE OF PERCHLORIC (0.6 *M*) OR SULFURIC (0.3 *M*) ACID ON THE MECA RESPONSES FROM PHOSPHORUS SALTS

| Compound | Intensity (mV/ng P) | |
|---|---|---|
| | 0.6 *M* $HClO_4$ | 0.3 *M* $H_2SO_4$ |
| $H_3PO_4$ | 0.16[a] | 0.47 |
| $Na_2HPO_3 \cdot 5H_2O$ | 0.40 | 0.48 |
| $NaH_2PO_2$ | 0.42 | 0.50 |
| $Ba(H_2PO_2)_2$ | 0.16 | — |
| $Na_4P_2O_7 \cdot 10H_2O$ | 0.40 | 0.50 |
| $Na_5P_3O_{10} \cdot 6H_2O$ | 0.41 | 0.52 |
| $Ca_3(PO_4)_2$ | 0.00 | 0.52 |
| $(NH_4)_2HPO_4$ | 0.17 | 0.45 |
| $K_3PO_4 \cdot H_2O$ | 0.43 | 0.46 |
| $Na_2HPO_4$ | 0.45 | 0.47 |

*Note:* Flame: 5.3 *l* $H_2$ $min^{-1}$, 4.2 *l* $N_2$ $min^{-1}$, 5.4 *l* air $min^{-1}$; cavity = stainless steel with silica liner; $t_m$ = 10 sec for all compounds.

[a] Intensity = 0.45 mV without acid added.



line molybdate method. It should be noted that the MECA procedure does not require prehydrolysis of the polyphosphates, as this is achieved in the cavity.

A number of aliphatic and aromatic phosphorus compounds dissolved in ethanol and benzene, respectively, have also been studied in stainless steel and aluminum cavities by measuring their HPO emission.[39] The effects of the solvents used on the intensity of the emission and on the $t_m$ values were studied in detail with the conclusion that as for $S_2$, HPO emission is seriously quenched by organic matter in the cavity if both analyte and solvent volatize simultaneously.

For these compounds, the sensitivity was found to depend on factors such as the nature of the compound (boiling point, composition, etc.), the solvent, and the cavity material. In most cases, better sensitivities were obtained in ethanol, using aluminum rather than stainless steel cavities. The order of sensitivity was generally phosphines $\geq$ phosphine oxides $>$ phosphites $>$ phosphates, the sensitivity thus increasing with decreasing oxygen content of the compounds. This is probably a consequence of the strong bonds formed between phosphorus and oxygen (P=O = 140 Kcal $mol^{-1}$; P–O $\simeq$ 95 Kcal $mol^{-1}$) being difficult to break in the cool MECA flame, while the much weaker P–C bond ($\simeq$ 63 Kcal $mol^{-1}$) ensures much easier breakdown to produce HPO. Under optimum conditions, sub-ng amounts of organophosphorus compounds can be determined indicating that MECA can probably be applied to the determination of phosphorus in biological samples, plastics, petrol, pesticides, fungicides and herbicides, etc.

Each organophosphorus compound has a characteristic $t_m$ value under defined conditions; therefore it is possible to resolve mixtures of compounds with sufficiently different $t_m$ values. For example, trimethyl phosphate ($t_m$ = 2.0 sec) has been separated from di-(2-ethylhexyl) phosphate ($t_m$ = 11.5 sec), tritolyl phosphate ($t_m$ = 9.0 sec), or triphenyl phosphate ($t_m$ = 7.0 sec) (Figure 27). However, in the last example, there was slight overlapping of peaks indicating that a $t_m$ difference of about 6.0 sec is necessary to solve peaks from nanogram amounts of such phosphorus compounds. A

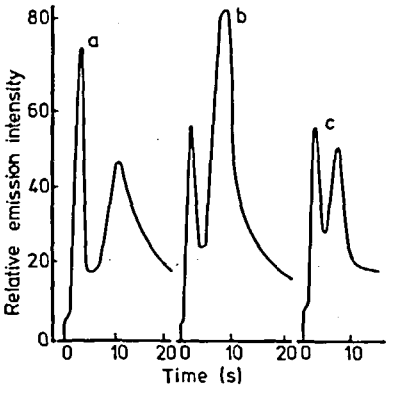



FIGURE 27. Emission responses from a mixture of trimethyl phosphate (100 ppm P) and (a) di-(2-ethylhexyl) phosphate (40 ppm P), (b) tritolyl phosphate (80 ppm P), and (c) triphenyl phosphate (60 ppm P).



ternary mixture of phosphorus compounds, e.g., trimethyl phosphate ($t_m$ = 2.0 sec), triphenyl phosphate ($t_m$ = 7.0 sec), and di-(2-ethylhexyl) phosphate ($t_m$ = 11.5 sec), showed overlapping peaks (Figure 10c); only the trimethyl phosphate peak could be resolved. The effect of water-cooling on these separations has been described above.

*4. Selenium and Tellurium*

The determination of selenium and tellurium by most flame techniques using direct aspiration is relatively insensitive and subject to numerous interferences.[68] Aspiration of an aqueous solution of selenium dioxide into a $H_2/N_2$ or $H_2/N_2$/air flame gave no emission attributable to a selenium-containing species, while an aqueous tellurium solution gave only a faint blue emission.[38] However, when selenium metal was placed as a powder into the MECA cavity and the $H_2/N_2$ flame ignited, a weak blue emission was observed. The intensity of the emission was greatly increased by adding air to the flame; the spectrum consists of a large number of bands, superimposed on a continuous background emission. Other selenium compounds, such as selenium dioxide or selenates, exhibit the same emission spectrum (Figure 28) attributed to $Se_2$.[69]

Different selenium compounds, although giving the same emission, behave differently.[32] For example, selenium powder exhibits two peaks ($t_m$ = 0.5 sec and 5.5 sec) in a hot flame (5.0 $\ell$ $H_2$ $min^{-1}$, 5.0 $\ell$ $N_2$ $min^{-1}$, and 5.5 $\ell$ air $min^{-1}$) while all the other selenium compounds ($SeO_2$, $Na_2SeO_3$, or $Na_2SeO_4$) under the same conditions exhibit only one peak, $t_m$ = 2.0 sec (Figure 29). Where air is not added to the flame, the $t_m$ values increase as expected (for example, for $SeO_2$ from 1.9 to 3.1 sec). Addition of phosphoric acid or ammonium phosphate to the solutions of selenium has no effect on the $t_m$ values, but the peaks were three times more intense. The slope of the log (intensity)-log (amount of selenium plots) was 1.6, confirming the involvement of $Se_2$ as the emitting species. The use of a carbon cavity was found to give more sensitive results, and the $t_m$ values were smaller ($t_m$ = 1.2 sec).

The emission-time response varies with the constitution of the selenium compound; thus separate calibration graphs are necessary for each compound introduced into the cavity. Conversion of selenium compounds to a single form might be a convenient means of determining total selenium and of removing all interferences. Selenium can be precipitated as the element using an appropriate reducing agent, e.g., sulfur dioxide

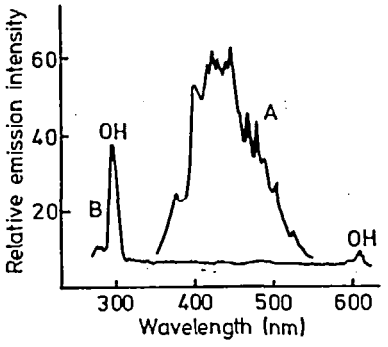



FIGURE 28. MECA spectrum obtained from (A) selenium dioxide in a $H_2/N_2$ flame, (B) flame background. (From Belcher, R., Bogdanski, S. L., Knowles, D. J., and Townshend, A., *Anal. Chim. Acta*, 79, 292 (1975). With permission.)

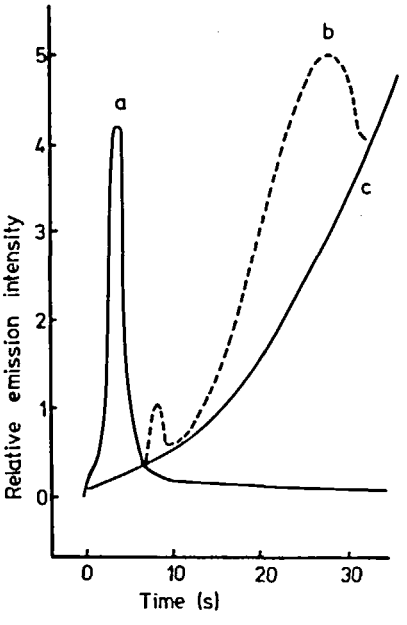



FIGURE 29. MECA responses from (a) selenous acid (1 μg Se); (b) telluric acid (6 μg Te); (c) incandescent background, stainless steel cavity, 500 nm. (From Belcher, R., Bogdanski, S. L., Knowles, D. J., and Townshend, A., *Anal. Chim. Acta*, 79, 292 (1975). With permission.)

or hydroxylammonium chloride. The metal is filtered off through a small glass-fiber filter. The emission obtained when this paper is placed in a cavity and introduced into the flame is recorded as with direct injection. The precipitation technique was applied to the determination of selenium in "selenium sulfide" reported to contain 41 to 42.5% selenium and to synthetic solutions of small concentrations (0.4 to 0.8 μg mℓ

(4 μg) of selenium in 5 mℓ of concentrated sulfuric acid.[33] For organoselenium compounds where the interferences were due to the organic matrix and not to a specific element, the samples were burned in an oxygen flask and the resulting solution measured by direct injection into the MECA cavity. Using aqueous selenium dioxide solutions as standards, very small concentrations (0.02 to 0.4%) of selenium in shampoo formulations and organoselenium compounds were determined very rapidly.[33]

Tellurium compounds ($TeO_2$, $H_4TeO_6$) showed a bright green emission coming from the cavity space, while a faint blue emission occurred in the flame above the cavity.[33] The green emission spectrum, with a maximum around 500 nm, was observed previously and is probably due to $Te_2$ rather than TeO,[70] on the basis of the log-log slope of 1.8.[32]

As the cavity containing a tellurium compound heats up in the flame, two peaks occur. The first peak is very small; the second is much more intense, but is superimposed on the incandescent emission of the stainless steel cavity (Figure 29). Using a carbon cavity, the main peak occurs well before the incandescence emission of the cavity. The peak is greatly intensified in the presence of organic compounds such as ascorbic or citric acid. The detection limit was 1 μg Te and 0.6 μg Te as telluric acid in 5 μℓ aqueous solution and citric acid solutions, respectively.[32]

The calibration graphs for selenium and tellurium are "S"-shaped, with a fairly linear range between 200 to 450 ng Se and 5 to 12 μg Te, respectively. The slopes of the log-log plots were 1.6 and 1.8 for selenium and tellurium, indicating as for sulfur compounds that the emitting species are $Se_2$ and $Te_2$.

*5. Halogens*

Although the halogens themselves give no emission in the MECA cavity, the presence of certain metals or their salts in the cavity stimulates very sensitive emissions derived from MX (M = Cu, In, Sn, Ga, Ge, Mn, Co, Ni, or Pb; X = Cl, Br or I).

In aspiration systems only Cu,[71] In,[72,73], Sn[74], and Ga[73] have been found to give significant MX emissions, together with simple metal oxide, hydroxide, and hydride emissions, which in most cases produce spectral overlapping problems. In the cavity, however, the emission arises mainly from the metal(I) halide and there is often very little contribution from oxy-species (see description of tin above). This is attributed to the fact that the inner surface of the cavity is cooler than the rest of the flame and the concentration of flame radicals is not great; this discourages the formation of oxides and hydroxides. For example, copper(II) chloride solution aspirated into a $H_2/N_2$ diffusion flame behaves quite differently from when it is injected into a MECA cavity placed in the same flame. The spectra obtained (Figure 30) are very different; in the cavity, the reduced intensity of the CuH, CuOH, and CuO bands is noticeable as are the greatly enhanced bands attributed to CuCl emission.[5] Copper(II) bromide and iodide give significantly different spectra in the cavity. By measuring the emissions at 488 nm (CuCl), 480 nm (CuBr), and 509 nm (CuI), nanogram amounts of the halides can be detected.

*a. Indium*

When using indium instead of copper, more sensitive InX emissions have been obtained. The presence of indium in the cavity can be achieved either by adding indium(III) ions to the test solutions[10] or by using an indium-plated cavity.[75] The use of the latter, although giving very sensitive emissions, has some disadvantages. First, indium from the cavity surface is consumed and the cavity has to be treated from time to time to avoid a decrease in the intensity. Second, indium melts at 157°C, so it is difficult to have a homogeneous cavity surface coating. Finally, there are still some spectral overlapping problems, especially from $In_2$ emissions (as with aspiration sys-

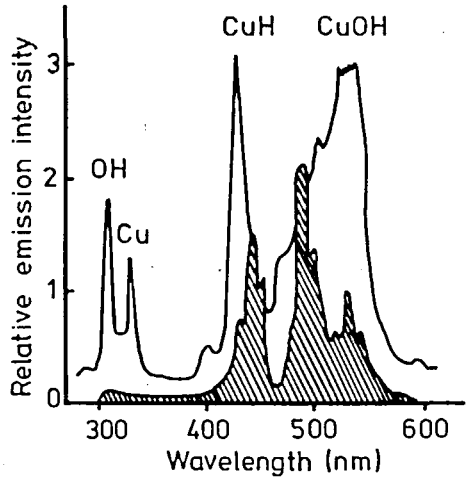



FIGURE 30. Spectra from an aqueous copper(II) chloride solution aspirated into a $H_2/N_2$ diffusion flame (line drawing) and in the MECA cavity in the same flame (solid drawing). (From Belcher, R., Bogdanski, S. L., Ghonaim, S. A., and Townshend, A., *Nature (London)*, 248, 326 (1974). With permission.)

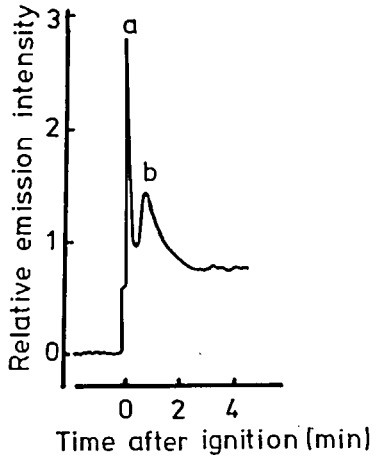



FIGURE 31. Emission-time response for (a) InCl and (b) $In_2$ at 360 nm. (From Stiles, D. A., *Proc. Soc. Anal. Chem.*, 11, 141 (1974). With permission.)

tems). This, however, is diminished by keeping the temperature of the cavity as low as possible; $In_2$ emission is separated from the Inx emissions because of differences in $t_m$ (Figure 31).

A more reliable way, at present, of producing indium(I) halide emissions is by preparing halide solutions containing indium(III) nitrate and injecting aliquots of the resulting solutions into the cavity followed by the measurement of the emission produced at the appropriate wavelength when the flame is ignited[10] Chloride, bromide, and io-

dide samples all showed a two-peaked response: the first, sharper peak occurring at 12 sec after igniting the flame, attributed to an InX species, the second, broader peak, occurring after 40 sec, related only to indium (Figure 31). The second peak was obtained alone when a sample containing only indium nitrate was introduced into the cavity. However, its appearance was avoided if the flame was extinguished immediately after the first peak appeared. This ensured the presence of an excess of indium in the cavity and thus repeatable conditions for halide determinations. The indium(I) halide emission intensity was directly proportional to the halide concentration, and the detection limits achieved under optimal conditions were 2.5 ng for chloride and bromide and 50 ng for iodide.

Severe depressive interferences have been found from cations, especially alkali and alkaline earth metal ions which form more strongly bound halides, thus preventing the formation and vaporization of indium halides. Some anions, such as sulfate and phosphate, added in large amounts also decrease the emission, probably by forming salts with indium(III) which prevent indium from reacting with the halide. The precipitation of halides as silver salts has been found to be useful for avoiding these interferences. The precipitate was collected on a filter paper, redissolved in ammonia, and the halide determined. This is also a means of concentrating the halide, thereby increasing the overall sensitivity.

The three halides mutually interfere in the determination of one another at large slit widths as a result of spectral overlapping. Such effects are greatly reduced by decreasing the slit widths, but at the expense of sensitivity.

The procedure used for stimulating InX emissions has been applied to the determination of ppm amounts of chloride in tap water using a standard addition procedure, without a preseparation step. However, for samples with high cation concentration, the results obtained by MECA were lower than those given by a chloride meter.[10]

The determination of some organic chlorides such as monochloro-, dichloro-, and trichloro acetic acid as well as hydroxylammonium chloride and L-cysteine hydrochloride via the measurement of InX emission has been established by direct injection of the solution into an indium-lined cavity.[76] Organochlorine pesticides (e.g., *p,p'*-DDT, γ-BHC, and heptachlor) in sediments have been also determined by MECA. After extraction from the sediment, chlorine was liberated as hydrogen chloride in an oxygen flask.[77] The resulting aqueous solutions were injected into an indium-lined MECA cavity and the response used to determine the amount of halogen in the sediment in the range 5 to 25 μg $ml.^{-1}$. The above procedure was modified to allow a sample of dibromochloropropane to be analyzed.[78] After ignition in the oxygen flask, the resulting solution was made basic with ammonia and the resulting ammonium halide separated by thin layer chromatography on cellulose. The separated components were dissolved in water and analyzed by MECA using the InBr and InCl emissions, respectively. Experiments were also conducted to gauge the effectiveness of the separation procedure on samples of nemagon, maloran, mixtures of ethylene dibromide and ethylene dichloride, terbacil, and bromacil In all cases the recovery was estimated to be greater than 90%. These compounds also give InX emissions when introduced directly into an indium-plated cavity.

### *b. Gallium*

As for indium, gallium was found to give molecular emissions when added in excess to a solution of bromide or iodide.[59] Unlike the indium halide, however, the emission of gallium(I) bromide at 350 nm was less sensitive than that of gallium(I) iodide at 391 nm. The detection limits obtained were 0.6 μg Br and 0.25 μg of iodide. However, the presence of iodide ions in the bromide solution considerably increased the GaBr emission, making possible the determination of as little as 50 ng of bromide. A possible

explanation of this effect is that a mixed halide, e.g., $GaI_2Br$, is formed, which is more volatile than $GaBr_3$ and therefore is obtained more rapidly in the vapor phase. As the Ga–Br bond is stronger than the Ga–I bond,[79] GaBr is formed as the emitting species.

*c. Tin*

Small amounts of tin(II) chloride or bromide in the cavity produce broad emission bands with peaks at 440 and 460 nm, and 460, 480, 490, and 495 nm, respectively. These do not correspond to the red SnH or blue SnO emissions, but appear to be similar to the blue-green emission that appears at the base of the hydrogen diffusion flame when tin(II) halide is aspirated (Figure 1) and is therefore attributed to tin(I) halide emissions. Iodide however, gave rise to only a faint red emission, probably SnH.[65]

For the stimulation of SnCl and SnBr emissions, a tin-plated cavity or test solution containing tin salts can be used. However, only SnCl emission has been used for analytical purposes, which permitted the determination of chloride at ppm levels.[65]

Much greater sensitivity and the possibility of determining all three halides was achieved by using a tin-plated oxy-cavity.[11] The introduction of oxygen to the cavity promoted the formation of SnO emission with maximum intensity at 485 nm. Resolution of the halides was achieved on the basis of the different volatilities of their tin salts (Figure 32), but some interference was observed with changes of $t_m$ value for certain halide combinations, probably because of volatilization of mixed halides, e.g., SnClBr. Thus, simple separation techniques must be used prior to measurement of emission when a mixture of halides is present. Iodide can be selectivity eliminated by treating the binary mixture (chloride or bromide with iodide) with nitrous acid:

$$4H^+ + 4I^- + 2NO_2^- \rightarrow 2I_2 + 2NO + 2H_2O \qquad (24)$$

The iodine formed is volatilized by gentle warming of the solution. Bromine and iodine are volatilized from a mixture with chloride by warming the solution containing lead dioxide and glacial acetic acid:

$$2H^+ + 2Br^- + PbO_2 \rightarrow Br_2(I_2) + Pb^{2+} + 2H_2O \qquad (25)$$

The detection limits achieved were 5.5 ng of $Cl^-$, 4.0 ng of $Br^-$, and 32 ng of $I^-$. Not only can the halides be determined in the presence of the metals forming metal(I) halide emissions, but the metals themsleves can be quantitatively, but generally not sensitively, determined using excess halides.

*6. Tin*

The tin(I) halide or SnO emissions promoted by injecting halide solutions into a tin-plated cavity or tin-plated oxy-cavity, respectively, were initially used only for the determination of halides.[3,65] For the determination of tin, however, a number of inorganic tin compounds (e.g., tin(II) halides, tin(IV) halides, sulfide, nitrate, and sulfate) in aqueous or nonaqueous solutions were injected into an aluminum, water-cooled oxy-cavity and the resulting SnO emission measured at 585 nm.[80] The tin in these compounds can be determined with different sensitivities and the $t_m$ value for each compound varies with volatility. Table 4 gives the characteristics of some tin compounds studied, showing that based on the difference between their $t_m$ values, certain mixtures of inorganic tin compounds can be resolved. Figure 33 shows that the minimum $t_m$ difference required for complete separation is 5 sec under the conditions used.

Based on the same principle, certain organotin compounds were determined after evaporating the organic solvent from the cavity.[80] The intensity of the emission ap-

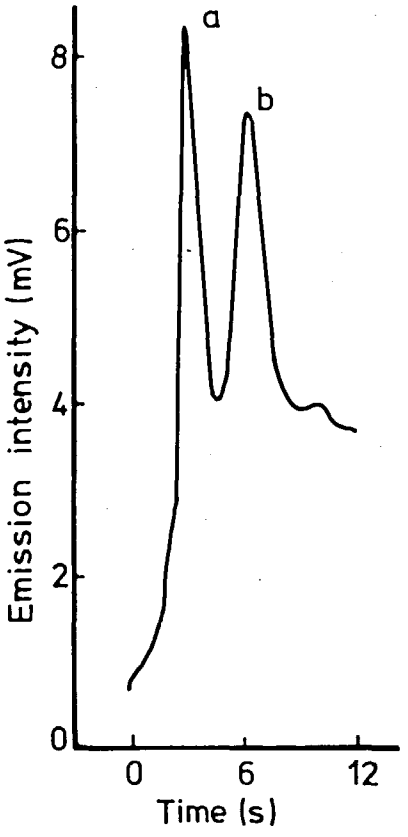



FIGURE 32. MECA responses obtained in a tin-plated oxy-cavity by measuring the SnO emission intensity from (a) tin(II) chloride (10 ppm Sn) and (b) tin(IV) bromide (5 ppm Sn).

peared to be independent of the nature of the solvent and was $R_4Sn < R_3Sn < R_2Sn$, the peaks becoming broader and shorter with increasing mass of the organic component. It appears, with few exceptions, that the lower boiling oint compounds show higher sensitivity (as measured by peak height) than the higher boiling point compounds. These compounds may be determined in the ng range as required for determination of organotin compounds in wood preservatives, paint additives, disinfectant sprays, and some medicines. Some speciation is again possible (Figure 33).

A different way of producing SnCl emissions has recently been developed using the so-called "HCl-cavity".[6] Tin(II) chloride solutions in dilute hydrochloric acid were injected into a carbon cavity, and gaseous hydrochloric acid was introduced through a hole in the back wall of the cavity. The blue tin(I) chloride emission so generated was measured at 440 nm. Corrosion by hydrochloric acid of the stainless steel tubing and of the valve of the cylinder make this procedure irreproducible. Thermal decomposition of magnesium chloride ($MgCl_2 \cdot 6H_2O$) within the cavity for hydrochloric acid generation improved the reproducibility and made possible the determination of tin down to 0.5 ng. However, using a hydride generation technique (see below) the sensitivity was ten times greater, and the fewer interferences from some cations were overcome by simply adding EDTA before generating the gas.[9]

Table 4
MECA CHARACTERISTICS OF SOME TIN COMPOUNDS

| Compound | $t_m$ (sec) | Detection limit (ng Sn) | Sensitivity (mV/ng Sn) |
|---|---|---|---|
| Monooctyltin trichloride | 3 | | 0.16 |
| Dibutyltin dichloride | 3 | | 0.07 |
| Dibutyltin oxide | 10 | 0.025 | 0.29 |
| Dibutyltin maleate | 3 | 0.25 | 0.26 |
| Dibutyltin oxalate | 8 | 0.25 | 0.11 |
| Dibutyltin dibenzoate | 3 | | 0.12 |
| Tributyltin chloride | 6 | 0.5 | 0.16 |
| Tributyltin oxide | 7 | 2.5 | 0.10 |
| Triphenyltin acetate | 7 | 0.5 | 0.17 |
| Tetrabutyltin | 4 | | 0.08 |
| Tetrabutyl distanno diacetate | 5 | | 0.18 |
| Tin(II) chloride | 5 | 0.25 | 0.90 |
| Tin(II) bromide | 6 | 0.25 | 0.19 |
| Tin(IV) bromide | 8 | 0.25 | 0.18 |
| Tin(IV) chloride | 3 | 0.25 | 0.16 |
| Tin(IV) iodide | 15 | 2.5 | 0.09 |
| Tin(IV) sulphide | 7 | 1.3 | 0.12 |
| Tin(IV) nitrate | 9 | 1.3 | 0.14 |

*Note:* Flame (organo tin compounds): 2.5 *l* $H_2$ $min^{-1}$, 5.5 *l* $N_2$ $min^{-1}$, no air; (inorganic compounds): 3.0 *l* $H_2$ $min^{-1}$, 5.5 *l* $N_2$ $min^{-1}$, 4.0 *l* air $min^{-1}$. Water-cooled aluminum oxy-cavity, 90 m*l* $O_2$ $min^{-1}$.

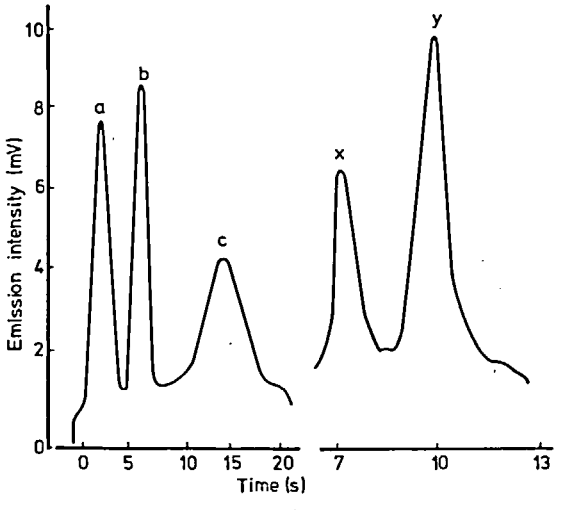



FIGURE 33. Resolution of (a) tin(IV) chloride, (b) tin(IV) bromide, (c) tin(IV) iodide (5 ppm Sn each); (x) tributyltin oxide, and (y) dibutyltin oxide (5 ppm Sn each).

*7. Boron*

Boron compounds introduced into a hydrogen flame give a green $BO_2$ emission. Because of the high temperature required to achieve decomposition and complete volatilization of boron compounds, the sensitivity achieved by injecting aqueous borate

solutions into an oxy-cavity was poor;[8] the emission could not be observed satisfactorily as a steel cavity incandesces before any boron emission occurs. A more volatile boron compound is formed by solvent extraction in which boron is chelated with 2-ethylhexane-1,3-diol and extracted into methyl isobutyl ketone from acidic solutions.[8] Aliquots of the extract were injected into the oxy-cavity, and the emission measured at 518 nm. The effect of the organic solvent was eliminated by evaporation before the introduction of the cavity into the flame. Linear calibration graphs were obtained over the range 5 to 80 ng of boron, with a standard deviation of 4%. Another means of producing more volatile boron compounds (methyl borate[8] or boron trifluoride[34]) is used in a volatilization system (see below).

*8. Indium and Gallium*

Indium(I) halide emissions were found to be very sensitive, and indium can be determined sensitively on this basis. Injection of gallium solutions into a carbon cavity gave measurable emissions only if they contained excess of bromide or iodide.[59] Emissions from solutions containing gallium in the presence of chloride or fluoride were not obtained. The emissions attributed to GaBr and GaI gave maximum intensity at 350 nm and 391 nm, respectively. Because of its higher sensitivity, GaI was used for the determination of gallium with a detection limit of 0.5 ng Ga.



*9. Germanium*

Germanium solutions prepared in hydrochloric acid give an intense blue emission when injected into a carbon cavity placed in an $H_2/N_2$ flame.[59] The same emission was obtained from germanium solutions prepared in ammonium perchlorate, ammonium chloride, or perchloric acid solutions, suggesting that the same emitting species (GeCl) is responsible. In the presence of ammonium bromide, germanium gave a very weak, irreproducible green emission, while in the presence of fluoride or iodide no emission was detected. Measuring the maximum GeCl emission intensity at 455 nm, and using an excess of hydrochloric acid, a detection limit of 10 ng of Ge was achieved. Most cations depressed the germanium emission by consuming the chloride to form less volatile compounds or themselves giving metal halide emissions, completely masking that from germanium chloride. Some anions, such as phosphate, sulfate, nitrate, and iodide, also suppressed the emission from germanium. The effect of interfering ions was eliminated by solvent extraction of germanium tetrachloride from hydrochloric acid into carbon tetrachloride[81] and injection of the extract into the cavity. This procedure is also slightly more sensitive than those using aqueous solutions.

*10. Copper*

Direct determination of as little as 0.5 μg of copper was accomplished by employing the "HCl-cavity and the procedure described for tin (see above).[6] Also by measuring the CuCl emission, copper was determined in steel samples[82] directly after dissolution in $HCl-HNO_3$, using a standard addition procedure.

Indirectly, copper has been determined via the $S_2$ emission from its diethyldithiocarbamate chelate or *in situ* after formation of copper sulfide in a silica-lined stainless steel cavity (see above).[40]

*11. Other Metals*

The $S_2$ emission from dithiocarbamate and similar chelates of some metal ions has been noted above. Manganese(II), cobalt(II), nickel(II), and lead(II) were found to emit metal(I) halide (other than fluoride) spectra from the MECA cavity in a $H_2/N_2$/air flame.[4] These emissions are not observed in aspiration systems using the same flame. Table 5 gives the most intense emission wavelengths forthe metal halides stud-

Table 5
WAVELENGTHS OF MAJOR MECA PEAKS FOR SOME METAL HALIDES

| Compound in cavity | Wavelength of most intense peak (nm) |
|---|---|
| $MnCl_2$ | 500 |
| $MnBr_2$ | 507, 545 |
| $MnI_2$ | 495, 562 |
| $CoCl_2$ | 500 |
| $CoBr_2$ | 490 |
| $CoI_2$ | 535 |
| $NiBr_2$ | 473 |
| $FeCl_2$ | 365, 515 |
| $PbCl_2$ | 485,500 |
| $PbBr_2$ | 502 |
| $PbI_2$ | 485, 500, 522 |



ied. The presence of hydrogen halide molecules inside the cavity and the low temperature and low content of oxy-species of the flame promotes the formation of metal(I) halide molecules, discouraging the formation of other molecules or of most atoms. Some of those spectra, however, also contain atomic emissions, e.g., Fe at 365 nm, Co at 345 nm, and Mn at 403 nm. All the atomic emissions except probably manganese are too weak under MECA conditions to have any analytical use. Cadmium, thallium, sodium, potassium, and lithium, however, give only atomic emissions in the MECA cavity.

A cavity containing a cadmium(II) halide, introduced into a hydrogen-nitrogen flame shows an intense cadmium atomic emission at 326.1 nm.[7] Introduction of oxygen directly into the cavity in an attempt to increase the atomic emission intensity completely suppressed the atomic emission probably because of the production of CdO at the expense of cadmium atoms. However, CdO emission could not be detected, so it is possible that the molecule is not formed in an excited state. Different sensitivities and $t_m$ values were obtained for different cadmium compounds. There seemed to be a direct relationship between sensitivity and volatility as well as the bond strength of some cadmium halides. The atomic emission intensity is unusually high considering the low temperature at which it occurs (e.g., 600°C).

Many cations and anions were found to suppress the emission from cadmium atoms, probably as a result of formation of less volatile compounds with the analyte. Most of these interferences, however, could be eliminated by using a hotter flame (i.e., with added air) and employing a stainless steel cavity insulated from the cavity holder with a ceramic ring which minimizes transference of the heat from the cavity. Under these conditions only sulphate, phosphate, and silicate were found to still delay the emission and broaden the peaks because of slower volatilization. Addition of sulfuric acid to the test solutions converts all the salts to the sulfate so that $t_m$ values and sensitivities are unaffected by the presence of other anions. This enables nanogram amounts of cadmium to be determined very quickly.

Thallium gives a green atomic emission, measurable at 377.5 nm, in an oxy-cavity. A linear calibration range of 0.025 to 2 ng and a detection limit of 5 ng of thallium were achieved.[9] A number of ions (especially $K^+$, As(III), Sb(III), Bi(III), and $Ga^{3+}$) interfered.

Lithium and potassium exhibit their characteristic[9] atomic emissions at 670.5 nm and 766.5 nm, respectively. Potassium also has an intense line at 404.5 nm. Because

the photomultiplier used for MECA was not sensitive for emissions over 700 nm, the measurements were made at 404.5 and 670.5 nm for potassium and lithium, respectively. The detection limits were 25 ng of potassium and 5 ng of lithium, each in 5 $\mu\ell$. This technique is not as sensitive as the conventional flame atomic emission or absorption methods commonly used for the determination of alkali metal. However, other workers[83] have used MECA to determine lithium, sodium, and potassium with detection limits of 0.7 ng, 2.3 $\mu$g, and 2.3 $\mu$g, respectively. This method was mainly developed for the determination of lithium in physiological samples during therapeutic treatment with lithium carbonate of subjects with human affective disorders. The simplicity of operation and small sample sizes make the method attractive for further development.

### B. Applications to Solid Samples

It has been shown on several occasions that the direct analysis of solid samples by MECA is possible, although there are some problems that have to be overcome. A few milligrams of the solid material can be placed in a cavity and the emission recorded as with liquid samples. The mode of addition and the amount of solid placed in the cavity, its particle size, matrix composition, and the nature of the residue left after the measurement of the emission are some of the factors which must be taken into account in order to obtain reproducible and accurate results.



The introduction of the solid material into the cavity and reproducible rotation into the flame have been accomplished in different ways. Use of a normal MECA cavity provides reproducible rotation into the flame, but the solid could not be spread homogeneously onto the surface of the cavity. Usually, the solid powder (e.g., coal) is suspended in acetone which, on drying, allows the coal to stick to the surface. This procedure has been applied to the direct determination of sulfur drugs in tablet samples.[12] The drug sample, carefully ground and sieved through a 60-mesh sieve, was weighed carefully (microgram amounts) and transferred to a carbon cavity. A drop of acetone was added to the cavity so that the powder adhered to the cavity wall. The solvent was allowed to evaporate for a few seconds and the cavity introduced into an $H_2/N_2$/air flame. When the emission ceased, the cavity was left in an $H_2$/air flame to remove any residue, cooled to room temperature, and used for the next experiment. The $t_m$ values and sensitivities decreased in the same order as with drug solution samples. The calibration was less sensitive than for pure drugs, probably because of the depressive effect of ingredients such as starch and magnesium stearate in the tablets. It is necessary, therefore, to prepare a calibration graph for the pure drug in the presence of added amounts of matrix ingredients. Accurate weighing of such small samples was also found to be difficult. As an alternative, a special cavity holder was designed to enable easy and reproducible change of the cavity during the analysis.[46] An aluminum block with a "groove" at one end was used for transferring reproducible known amounts of material to the cavity (few milligrams) without using a balance (Figure 34). This assembly has been used for the determination of sulfur in iron ores and blast furnace slags with a reproducibility of 6.5%. It has also been applied to sulfur in pitch. Care must be taken to use as little solid material as possible to avoid a large deposit of residue in the cavity which, by changing the active volume of the cavity, causes a decrease of the emission. The samples also must be finely powdered in order to give a homogeneous and readily decomposed mixture. Pure materials or materials of known concentration are required for the construction of calibration graphs, depending on the analysis.

The ability of conventional MECA to differentiate between compounds having a common element on the basis of their $t_m$ values was also found to apply to solid samples.[15] In fact, a solid powdered mixture of calcium sulfide ($t_m$ = 27 sec), calcium

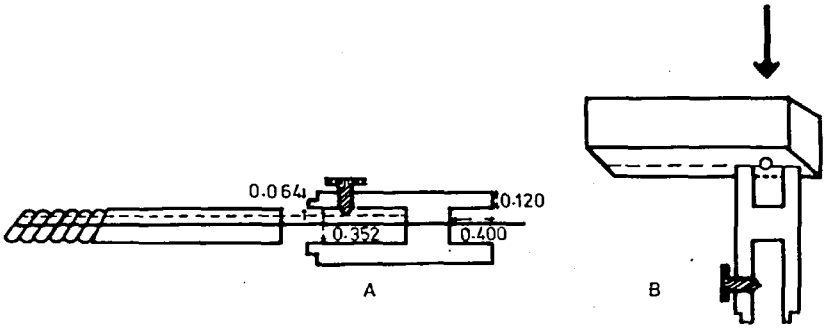



FIGURE 34. Cavity holder for analysis of solid samples (A) and aluminum block for transferring the sample into the cavity (B). Dimensions in mm.

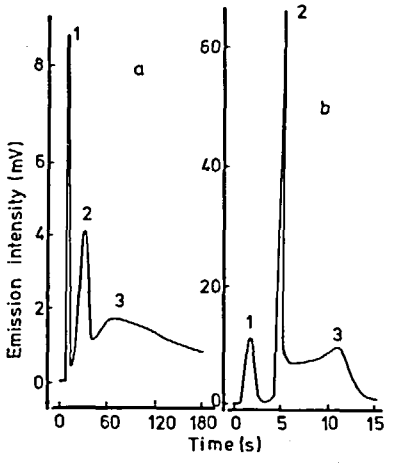



FIGURE 35. Emission responses from (a) a mixture of solids: (1) thiourea, (2) calcium sulfide, (3) calcium sulfate; (b) powdered coal with peaks from: (1) organic and pyritic sulfur, (2) pyritic sulfur, and (3) sulfate sulfur.

sulfate (45 sec) and thiourea ($t_m$ = 9 sec) shows a triple peaked response, where the $t_m$ of each compound in the mixture corresponds to that of the single compounds alone (Figure 35a). This was found to be very interesting for the identification of different chemical forms of sulfur in coal. Powdered coal gave a three-peaked response in the MECA cavity (Figure 35b). The peak with the largest $t_m$ is due to inorganic (mainly calcium) sulfate, the middle peak to pyritic (FeS) sulfur, an the first peak is also due to pyritic sulfur and the various organic sulfur species present. It is possible, therefore, to determine the various forms of sulfur very rapidly provided suitable standard coals are available. Results are good for standards and samples of the same type of coal.

For pitch samples containing natural sulfur and sulfur added to increase the coking yield, a quick method for measuring both types of sulfur can be established using synthetically made standards which incorporate the sulfur in the same manner that it exists in the sample. Finally, various lichen samples collected from polluted and unpolluted areas in France gave multipeaked responses for sulfur. There appeared to be

a correlation between the intensity of the sulfur emissions and the amount of pollution, but the peaks were not identified.

Recently, Fernando et al.[84] reported the use of MECA for simultaneously identifying and determining sulfite and sulfate in solids. The standards (~500 ppm in sulfur) were prepared by dispersing sodium sulfite or sodium sulfate in silicon dioxide, and mixtures were obtained by combining the above standards. Small aluminum foil cups were used for weighing and handling solid samples of the order of 0.2 to 3 mg. The solid was wetted with 0.01 *M* phosphoric acid or a mixture of 0.01 *M* phosphoric acid and Triton X-100 (~5 $\mu\ell$/100 m$\ell$). The cup was placed in a quartz-lined cavity and the emission measured at 383.6 nm. The calibration curves revealed linear ranges covering nearly two powers of ten ($10^{-5}$ to $10^{-7}$ g of sulfur) for either sulfite or sulfate. The technique was intended for use to determine sulfur anions in atmospheric particulates. Glass fiber filters which mimic the chemical and physical properties of the powdered silicon dioxide of the standards were used to collect the airborne solids. The filters were weighed before and after collection, placed in the cavity, and the emission measured as before.

A filter cavity has been designed[85] in which solids (precipitates, air particulates, etc.) can be collected, and the cavity then used directly for MECA of the solids. This avoids problems with transfer of the filter from the collection device to the MECA cavity.

Using a modified stainless steel cavity, Kouimtzis[35] has been able to determine sulfur dioxide in air by absorbing and thus concentrating the pollutant selectivity in silica gel pellets. When the pellets are placed in a suitably shaped cavity, the absorbed gas gives a typical peak, which allows the reproducible measurement of 5 to 120 ng of $SO_2$ with a detection limit of 3 ng of $SO_2$. Sulfuric acid mist and mercaptan vapors were found to increase the response from sulfur dioxide, since they are also absorbed by silica gel. Organic solvent vapors decreased the response; therefore, the air samples were passed through a tube containing magnesium perchlorate, glass fiber filter paper, and paraffin wax before absorption on silica gel. The results obtained by this procedure, applied to 0.5 $\ell$ of air, were in agreement with those obtained by applying the West-Gaeke method,[86] which required a 20.0-$\ell$ air sample.

A similar device was used for the determination of traces of sulfur in selenium.[87] The samples containing 2.5 to 60 ng of sulfur were combusted at 800°C and the sulfur dioxide evolved absorbed by silica gel and determined as above. Selenium dioxide, also evolved if absorbed on silica gel with sulfur dioxide, would result in a positive interference due to $Se_2$ emission. Selenium dioxide is removed, therefore, by absorbing it in a trap containing glass wool and glass fiber filter paper prior to the silica gel trap.

A method has also been established for the direct determination of sulfur in powdered teeth.[88] In samples of 1 to 3 mg of ground dentine, 0.01 to 0.03% of sulfur, probably as chondroitin sulfate, was determined.

## V. VOLATILIZATION SYSTEMS

The generation of the analyte as a volatile species for introduction into a flame for atomic absorption spectrometry is currently very popular for determining arsenic, antimony, selenium, tellurium, and a few other elements. These elements are converted to their hydrides, usually by borohydride reduction, and the gaseous hydrides are carried to the flame. Recently, such systems also have been applied to other spectroscopic sources such as the inductive coupled plasma.[89]

Similar systems have been developed for MECA. Often they are simple, give high selectivity, and great sensitivity. The procedure consists of direct vaporization of the analyte or conversion of the analyte into a volatile product by means of a chemical reaction. The gas generated in the reaction vessel (Figure 36 is a typical example) is carried to the cavity by a stream of oxygen or nitrogen. The volatilization system is

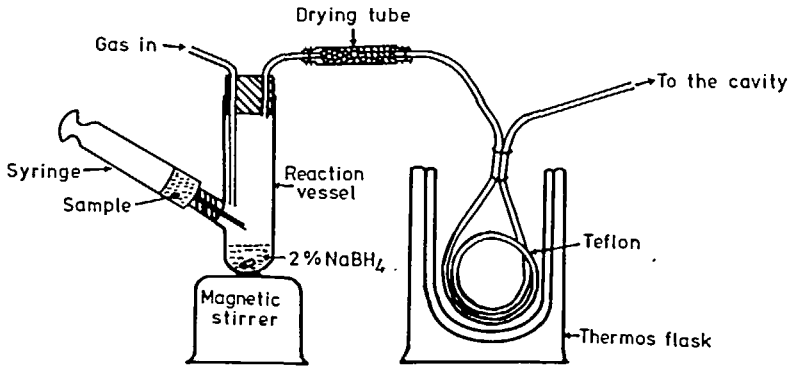



FIGURE 36. Volatilization system for generation of hydrides (the coiled Teflon® tubing is used as a cold trap or packed for gas chromatographic separation).

different from the conventional system in that the cavity is continually situated in the flame; thus the emission arises as soon as the gas arrives in the cavity.

When a chemical reaction is employed for the conversion of an analyte to a volatile product, several conditions must be satisfied. First it is necessary to use a reaction which avoids the formation of by-products which could interfere in the final measurements. Next there must be an efficient generation of the gas and, finally, the product obtained must be stable under the operating conditions before entering the cavity.

The elements determined using volatilization systems can be divided into two classes, based upon the emitting species.

1. Elements forming oxide emitters, e.g., boron, arsenic, antimony, tin, silicon, and nitrogen
2. Elements forming other emitters, e.g., sulfur, selenium, tellurium, iodine, and carbon

## A. Boron

The first element to be determined by MECA via a volatilization system was boron,[8] by generation of methyl borate. The gas was produced by the reaction of boric acid after evaporation of water with a mixture of methanol and sulfuric acid (5 + 1) at 80°C. The resultant $BO_2$ emission from an oxy-cavity measured at 518 nm was a broad, tailing peak recorded over 8 min. Although the procedure was found to be free of interferences, a considerable background emission from the blank (persistent blue CH emission in the cavity from excess methanol) prevented the detection of boron below 2 μg. The calibration graph was linear over the range 5 to 30 μg of boron.

The time of analysis was shortened by preparing boron solutions in methanol instead of water, so the evaporation step before generating the gas was eliminated.[34] Also the use of smaller generators (4.5 instead of 10 cm high) and a freezing trap (dry ice in mixture of chloroform and carbon tetrachloride) placed between the generator and cavity provided sharp peaks that were recorded over only 5 sec. The blank background was reduced considerably, and the detection limit achieved was 20 ng of boron in a 2-mℓ sample — lower than in the original system. The calibration graph was linear between 0.05 and 30 μg of boron. The method has been applied to the analysis of steels containing high (15%) or very low (0.001%) concentrations of boron, after dissolution in sulfuric acid and evaporation to dryness.

Boron can also be converted to boron trifluoride by heating a boron compound in the presence of excess fluoride with concentrated sulfuric acid.[34] The conditions used

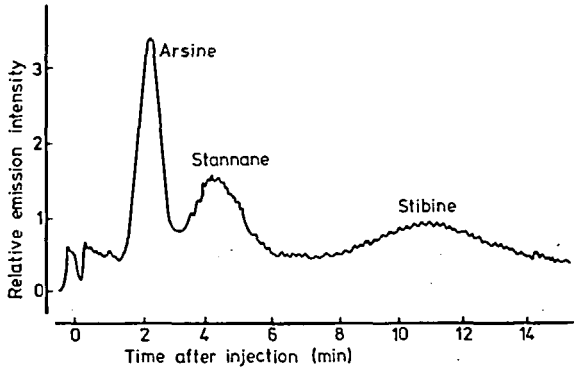



FIGURE 37. Separation of arsenic (10 μg), antimony (25 μg), and tin (25 μg) hydrides using 25-cm long Teflon® tubing packed with 10% silicone gum rubber on Porapak® Q at 9°C. (From Belcher, R., Bogdanski, S. L., Henden, E., and Townshend, A., *Anal. Chim. Acta*, 92, 33 (1977). With permission.)



for generating the gas and measuring the emission were those found to be optimal for the determination of silicon (see below); the sensitivity was lower than for methyl borate and the detection limit was 0.6 μg of boron. It is believed, however, that the development of a procedure for the determination of boron as its trifluoride under optimized conditions would considerably improve the sensitivity.

## B. Arsenic and Antimony

The injection of arsenic or antimony chlorides into an oxy-cavity placed in an $H_2/N_2$ flame generates a bluish-white emission, exhibiting broad, continuum spectra from 330 to 550 nm.[90] Both emissions were attributed to oxides. More intense emissions were obtained for those elements when their hydrides were generated and swept into the cavity. Generation of arsine and stibine was accomplished by using a borohydride reduction procedure,[91] achieving a working range of 0.4 to 5 μg of arsenic and about twice as much of antimony. The use of helium instead of nitrogen to dilute the hydrogen flame and as a carrier gas doubled the sensitivity for both. Arsenic and antimony mutually interfere as a result of almost complete spectral overlapping.

The procedure was further developed[49] in order to improve sensitivity and to remove interferences. The effect of most cationic interferences (Cu(II), Ni(II), Zn(II), Fe(III), Bi(III), Cd(II), Cu(II), and Ag(I)) was eliminated by making the test solution 0.01 *M* in EDTA.[92] Attempts were made to separate arsine and stibine by exploiting the difference between the boiling points of arsine (−55°C) and stibine (−17.1°C).[93] For example, a cold trap cooled by immersing it in acetone containing solid carbon dioxide (Figure 36) was used to collect stibine. Arsine was retained by a second cold trap which was cooled by liquid air. However, the procedure was impractical because stibine was only partially retained by the first trap.

A very efficient separation was obtained by means of a chromatographic column (10% silicone gum rubber on Porapak® Q) placed between the hydride generator and the MECA cavity.[49] The emission intensities from the corresponding oxides were measured at a single wavelength. Stannane, generated under the same conditions, could also be separated from arsine and stibine using the chromatographic column under slightly different conditions (Figure 37). The sensitivities (amount of analyte giving a 10-mm² peak area increment at a chart speed of 1 cm min$^{-1}$ at optimal instrumental sensitivity) were calculated to be 0.2 μg, 0.7 μg, and 0.75 μg for arsenic, antimony, and tin, respectively.

During hydride generation, a large amount of hydrogen gas is produced which greatly changes the background emission from the cavity. If the gas chromatographic procedure is used, hydrogen emerges from the column before the hydrides (Figure 37) and so does not affect the emission measurements. However, if only one hydride is generated, the chromatographic procedure can be replaced by a liquid nitrogen trap, which condenses the hydride and separates it from the hydrogen. The cold trap containing the concentrated hydride is then immersed in a water bath (40°C) and nitrogen (50 m$\ell$ min$^{-1}$) carries the gas quickly to the cavity. The sensitivities (minimum amount of analyte which gave a 0.1-mV increment in intensity while the flame background noise was 0.1 mV) for arsenic and antimony were 35 and 70 ng, respectively, which were better than those obtained with the original system[90] and with the gas chromatographic column.

Using the optimal conditions for the generation of silicon tetrafluoride (see below), arsenic was determined as its fluoride.[34] The detection limit was 0.3 $\mu$g of arsenic. The sensitivity could probably be improved by optimizing the working conditions with respect to arsenic.

### C. Tin

The experiment used for arsenic and antimony hydrides also allowed tin to be determined as its hydride ($SnH_4$). Further work has been carried out to optimize the conditions for tin.[9] It was found that by injecting a tin(II) solution prepared in 0.4 *M* hydrochloric acid into a generator containing powdered sodium borohydride (0.1 g), blue-white SnO emission was obtained in the oxy-cavity after the gas was released from the cold trap. The calibration graph was linear up to 50 $\mu$g of tin(II), and the detection limit was approximately 80 ng of tin(II) in 1.0 m$\ell$ of solution. Using tin(IV) solutions, the signal was 94% of that obtained from tin(II). Nickel(II) and cobalt(II) completely depresed the tin emission, pro y because they are preferentially reduced by sodium borohydride to the metal. This can either coprecipitate the tin, absorb the hydride formed, catalytically decompose it, or stop its evolution from solution. Bismuth(I) and tellurium(IV) also have a depressive effect on the emission, probably because they form volatile hydrides which react with tin in the cool flame. Arsenic(III) and antimony(III) showed strong positive effects because they form volatile hydrides which give strong emissions in the flame, overlapping the SnO emission at 408 nm. The suppressive effects from cations were eliminated by making the tin(II) solutions 0.02 *M* in EDTA. The hydride generation technique for the determination of tin is more selective and sensitive than the method used on conventional MECA which employs the HCl-cavity.[6]

### D. Silicon

Introduction of a volatile silicon compound into on oxy-cavity situated in a $H_2/N_2$ flame gives a white emission a uted to SiO.[34,94] The spectrum is a continuum, with high intensity and little structure between 540 and 620 nm.

An all-Teflon® volatilization system was used for the conversion of silicon to silicon tetrafluoride. Concentrated sulfuric acid was injected into the generator containing a small volume (0.2 m$\ell$) of the sample plus excess of a fluoride and chloride to speed the generation. The gas generated by heating the reacting mixture at 135°C was swept into an aluminum water-cooled oxy-cavity, and the resultant emission measured at 540 nm. The detection limit achieved was 0.5 $\mu$g of silicon in 0.2 m$\ell$ of sample solution. The procedure was satisfactorily applied to the determination of silicon (2 to 100 $\mu$g) in iron ores and rocks. The only serious interferents were arsenic and boron, which form fluorides under the same conditions and form the corresponding emitting oxides

when carried to the flame. Larger amounts (>1 mg) of some other elements were also found to interfere.

Because of the inconvenience of using chloride for quick generation of silicon tetrafluoride as well as the difficulty of handling the hot oil bath, the initial procedure was slightly modified.[34] Aqueous mixtures of silicate and fluoride (0.2 mℓ) were evaporated to dryness directly in the generators. After the addition of sulfuric acid, the generators were electrically heated at about 180°C for 5 min and the gas carried to a water-cooled aluminum oxy-cavity continually placed in a flame. Not only was the sensitivity and detection limit improved (detection limit = 0.3 μg of Si), but most of the interferences were eliminated by the introduction of the evaporation step and the absence of chloride. The procedure, apart from being sensitive and selective, is simple and easy to apply to many real samples, thus competing with most other flame techniques.

## E. Nitrogen

Various nitrogen compounds can be determined by MECA using a volatilization system to convert them into either nitrogen oxides[9] or ammonia.[48] The gases swept into an oxy-cavity placed in an $H_2/N_2$ diffusion flame produce a white emission recorded as an almost structureless continuum extending from 330 to 700 nm, with the maximum around 500 nm.



Nitrite and nitrate can be converted into nitrogen oxides by reacting with a reducing agent. For example, nitrite is converted to nitrogen monoxide by reaction with iodide in acidic media (Equation 24). The reaction is complete in 40 sec at 97°C and is not effected by most cations and anions. A suitable reducing agent will reduce nitrate to nitrite, which can then be further reduced to nitrogen monoxide. Zinc in the presence of manganese(IV) as a catalyst in alkaline solution gives a conversion of nitrate to nitrite of 85 to 90%. Other metals such as cadmium, copper, iron, and tin, gave good conversion yields of nitrate to nitrite in acidic media. The reaction is complete in 60 to 80 sec at 84°C. The detection limits for nitrite using the iodide method and nitrate using the zinc method were 1 and 2 μg of nitrogen, respectively.

The zinc procedure was also applied to the simultaneous determination of nitrate and nitrite. The emission from both ions is measured on one aliquot; nitrite is destroyed in another aliquot by addition of iodide and the emission from nitrate is measured as above.

A highly sensitive method has been developed for determining ammonia and ammonium ions.[48] The sample (0.05 to 0.2 mℓ) is injected onto three sodium hydroxide pellets (0.5 to 0.6 g) in a 4-mℓ glass vial, and the ammonia released carried by nitrogen via a heated tube to a water-cooled oxy-cavity held in an $H_2/N_2$ flame. The procedure is fast (<5 min per sample), is unaffected by other components including other nitrogen anions and urea, and gives a linear calibration response for solutions of up to 1.5% ammoniacal nitrogen (w/v). The limit of detection is 0.2 μg of ammonia (in 0.2 mℓ) and the coefficient of variation for determination of 100 ppm ammonia is 2%. The method has been applied to the rapid determination of water-soluble ammoniacal nitrogen in fertilizers (0.8 to 13%), river water samples (25 to 36 ppm), effluents, and coke oven liquors (130 to 4500 ppm). The results obtained by MECA compared well with the classical method (distillation of ammonia from alkaline solution, collection in excess standard hydrochloric acid, titration of unreacted hydrochloric acid) for fertilizers and with the quoted values for the other samples.[30]

The system can be extended to determine nitrate by including 30 mg of finely powdered Devarda's alloy with the sodium hydroxide. By a combination of the procedures described above, nitrite, nitrate, and ammonia could be determined.

Several visible emissions from simple nitrogen compounds have been observed in

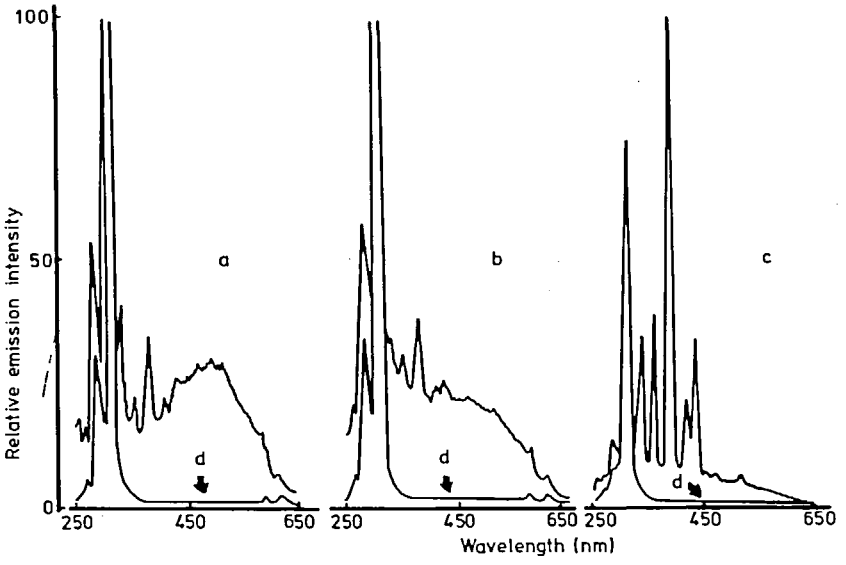



FIGURE 38. Emission spectra from: (a) methylamine, (b) dimethylamine, and (c) trimethylamine vapors when introduced into the MECA oxy-cavity; (d) is the flame background. (a,b) $N_2$ carrier gas = 35 m$\ell$ min$^{-1}$, $O_2$ supplied to the cavity = 45 m$\ell$ min$^{-1}$, (c) $N_2$ carrier gas = 35 m$\ell$ min$^{-1}$, $O_2$ supplied to the cavity = 98 m$\ell$ min$^{-1}$, slit = 0.2 mm (3.4 nm).



flames. These include the narrow NH band ($\lambda_{max}$ = 336 nm);[95,96] the $NH_2$ band (ammonia $\alpha$-band)[97,98] which covers the whole of the visible region with maxima at 664.2 630.2, 604.2, 571.3, and 543.6 nm,[99] as well as the NO–O continuum arising from the reaction:[100-102]

$$NO + O \rightarrow NO_2 + h\nu \qquad (26)$$

The last named extends from approximately 400 nm to the near IR and is strongest in the yellow and green regions.[99,103] Generally, when NO is introduced into a hydrogen flame, the NO–O continuum predominates if the oxygen concentration is fairly high and the temperature is <2500°K.[104] It is likely, therefore, that the nitrogen emission from the MECA cavity is mainly the NO–O continuum, perhaps with some $NH_2$ emission. This is supported by measuring the MECA spectrum from $ND_3$ under the same conditions. No change in wavelength or spectral distribution could be distinguished.[30]

Carbon compounds containing nitrogen show, in addition to CH and $C_2$ bands, emissions from NO, NH, and CN. The CN bands, in particular, have been used analytically, e.g., by Buell[105] and Dagnall et al.[95] to determine acetonitrile (detection limit = 60 $\mu g N m\ell^{-1}$) and Honma and Smith,[106] who determined various organic nitrogen compounds (detection limit = 0.8 mg $N$).

In the MECA oxy-cavity, NO, NH, and CN emissions can be clearly measured, together with the NO–O continuum, but the relative intensities of the various emissions depend on the compound.[30] For example, methylamine shows a large NO–O band with small contributions from NH and CN. Dimethylamine shows a decreased NO–O continuum, and trimethylamine has almost no NO–O continuum but much more intense CH and NH peaks (Figure 38). Ethylamine and propylamine gave no continuum, but these amines showed increased $C_2$ and CH emissions as well as more intense NH and CN peaks. Piperdine and pyridine show CH, $C_2$ and CN bands, but no NH band, probably because the breakdown process favors CN formation.[107] Like-

wise, acetonitrile and acrylonitrile both give CN bands which are more intense than the $C_2$, CH, and NH bands.

Compounds containing nitrogen and sulfur give emissions markedly dependent on the presence of oxygen introduced into the cavity. For example, in the absence of oxygen, isothiocyanatobenzene gives only the blue $S_2$ emission, whereas in the oxy-cavity prominent CN (but no NH) bands are observed.[30]

## F. Carbon

Carbon compounds give emissions mainly from CH and $C_2$, in the oxy-cavity, above a background that continuously rises from 300 to 650 nm, probably due to the HCO continuum. Acetaldehyde shows an intense CH emission as well as the $C_2$ band heads, whereas the introduction of dichloromethane (and other organochlorine compounds) gives enhanced $C_2$ bands as well as heads at 252 and 277 nm which might be CCl bands.[99]

Many carbon compounds can be converted to carbon monoxide or carbon dioxide in a volatilization system and one of the characteristic carbon emissions ($C_2$ or CH) recorded vs. time. Sensitivity, however, is rather poor.

## G. Halogens

Volatilization systems have been investigated only for the determination of iodine[108] and, indirectly, fluoride.[34,109] Iodine was evolved from an acidic iodide solution in the presence of dichromate. Nitrogen gas bubbling through the solution carried the iodine into an indium cavity and measured the resultant InI emission at 410 nm. This procedure awaits development.

Fluoride has been indirectly determined using the procedure described above for silicon.[34] The only modification was that an excess of silicon was used, the water was evaporated before sulfuric acid was added, and the generator was heated up to 180°C before passing nitrogen carrier gas through it. The complete evolution of the gas takes approximately 5 min and the SiO emission is measured at 540 nm. The detection limit was 5 μg of fluoride in 0.2 mℓ of solution. A study of some interferences revealed that all acids (nitric, sulfuric, phosphoric, and hydrochloric) added to the generators just before the evaporation step considerably decreased the intensity of the emission, probably because of the evolution of hydrofluoric acid. The interferences from acids were avoided by adjusting the pH to ≥7. Ammonium salts were expected to interfere with the measurements because ammonia vapors produce a white emission in the oxy-cavity (see above). However, because the fluoride solution together with the interfering ion in alkaline solution is evaporated to dryness, all ammonia is volatilized prior to the measurement. Arsenic and boron exhibit strong positive interferences because their trifluorides generated under the same conditions produced characteristic emissions. These interferences could not be completely removed, but were considerably decreased by measuring the SiO emission at 580 nm (where the contribution from AsO and $BO_2$ is small) with a slit width of 0.2 mm (≡ 13 nm).

The procedure for the determination of fluoride as silicon tetrafluoride (20 to 225 μg F) was successfully applied to the analysis of water and toothpaste samples. A spectrophotometric method (using alizarin fluorine blue[110]) was also used in order to validate the MECA findings for the samples chosen. The two methods gave consistent results; however, MECA is more rapid and free of most interferences from the sample matrix, especially from phosphate.

Further studies revealed that arsenic or boron could be used in place of silicon for the determination of fluoride. The detection limits were 1.6 and 10 μg of fluoride as arsenic and boron trifluoride, respectively.

## H. Selenium and Tellurium

Hydrogen selenide and telluride are evolved from strongly acidic solutions and the emissions obtained when the gases are swept into the cavity may be measured at 411 nm and 500 nm, respectively.[111] Selenium(IV) solutions, 2 *M* in hydrochloric acid, were injected into the generator containing 2% sodium borohydride solution and the gas collected in a liquid nitrogen trap which, after 2 min, was immersed in a hot water bath (90 to 95°C) to release the hydride. The detection limit was about 7 ng of selenium in 4 m*l* of solution. Using selenium(VI) solutions, no significant response was obtained, but after the reduction of selenium(VI) to selenium(IV) — boiling with concentrated hydrochloric acid for 5 min — the results were the same as those for selenium(IV).

Many elements were found to decrease the intensity of the selenium emission. Among these, lead, bismuth, and copper formed black suspensions (reduced by borohydride to metals), tellurium formed a black precipitate, and silver formed a white suspension (silver chloride) with a black tint. Other interfering ions, e.g., tellurium, arsenic, antimony, tin, germanium, and bismuth formed volatile hydrides after reaction with sodium borohydride. Tin, arsenic, and antimony completely depressed the selenium emissions in the cavity. They formed the corresponding hydrides which were swept into the cavity and gave the characteristic oxide emissions above the cavity. Tin also formed a red emission (SnH) inside the cavity, which caused spectral interference. Tellurium, sulfide, and sulfite caused a very serious positive interference by forming hydrogen telluride, hydrogen sulfide, and sulfur dioxide, which were carried to the cavity and gave $Te_2$ and $S_2$ emissions. Some of these interferences were simple to eliminate. Sulfide was oxidized by hydrogen peroxide to sulfate which does not interfere. Arsenic and antimony hydrides were evolved from a mixture with selenium by making first the solution 0.1 *M* in hydrochloric acid. Then, if the solution was made 2 *M* in hydrochloric acid, the emission from hydrogen selenide alone could be measured. Tin(II), bismuth(III), and germanium(IV) interferences could not be removed by the same procedure, probably because of the incomplete conversion to the corresponding hydrides. The effectiveness of the procedure was successfully tested for the determination of selenium in organoselenium compounds, after oxygen flask decomposition.



## I. Sulfur

A volatilization system for the determination of sulfur has been developed.[112] Hydrogen sulfide was generated by injecting a sulfide solution ($10^{-3}$ *M* in sodium hydroxide) into a generator containing 1.5 to 2.0 m*l* of 3 to 8 *M* hydrochloric acid. The gas was swept into a cavity placed in an $H_2/N_2$ flame after passing it through a drying tube to absorb any water vapors. The limit of detection for sulfide was about 40 ng when 1 m*l* of sample was injected and about 10 ng for a 50-$\mu l$ sample.

An improved procedure for generation of hydrogen sulfide has recently been developed. Many sulfur compounds, including sulfate, can be convertd by reduction with a reagent prepared by heating tin with anhydrous phosphoric acid.[113] If sulfate is added to the reagent in a volatilization generator and the reductant gradually heated up, $H_2S$ is released at approximately 200°C. The detection limit is approximately 1 ng of sulfur (in $\leq$1 m*l* of solution). Similar effects can be achieved with other sulfur anions and a sequential determination of up to four anions can be achieved based on their sequential evolution as the reductant temperature is varied.[31] This opens up large new areas for MECA development, not only for inorganic sulfur anions, which will be reported later.

Sulfite can be determined by evolution of sulfur dioxide from an acidic solution.[112] It can also be evolved from phosphoric acid solutions. A method was developed for the determination of sulfite in soft drinks using phosphiric acid.[114] Sulfur dioxide can be determined in the range 0.1 to 6 $\mu$g with a detection limit of 25 ng of $SO_2$.

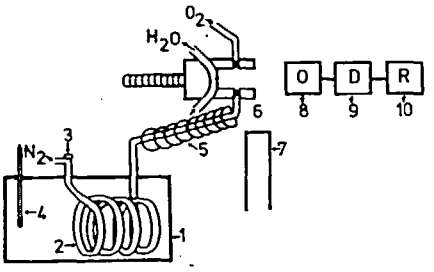



FIGURE 39. Diagram of the MECA chromatography system (not to scale). (1) air-circulated oven, (2) column, (3) injection port, (4) thermometer, (5) resistance tape, (6) duralumin water-cooled oxy-cavity, (7) burner, (8) optical system, (9), detector unit, (10) recorder.

## VI. MECA AS A GAS CHROMATOGRAPHIC DETECTOR

Based on the results presented above, it can be concluded that MECA provides high sensitivity and selectivity for a wide range of elements, mostly nonmetals. Its ability to monitor volatile compounds provided the incentive to use it in conjunction with gas chromatography as a multipurpose chromatographic detector.

The fact that oxide emitters (As, Sb, Sn, Si, N) give rise to broad bands in the region 400 to 600 nm permits the determination of two or more of those elements at a single wavelength after chromatographic separation. This was first applied to the separation of arsenic, antimony, and tin hydrides (Figure 37), which spectrally interfered in the determination of each other[49] (see above).

The separation of trimethyl and triethyl phosphates was monitored by MECA at 526 nm with an aluminum cavity in an $H_2/N_2$/air flame, using a column of 10% silicone gum rubber E-301 on Porapak® Q (50 to 80 mesh). A simple diagram of the system used is shown in Figure 39. (Oxygen was not supplied to the cavity.) The range of linearity was 0.05 to 0.85 μg P and 0.05 to >1.3 μg P for trimethylphosphate (peak height) and triethylphosphate (peak area), respectively. The separation of isopropyl sulfide and isopropyl disulfide was achieved with the same column. The slopes of the log-log plots were 1.88 for isopropyl sulfide and 1.96 for isopropyl disulfide,[41] compared with a requirement of 2.0 for a second-order rate dependence for excited $S_2$ formation. As a further example, thionyl chloride, carbon disulfide, and 2-methyl thiophene were separated (Figure 40) using a column of 10% SE-30 on Chromosorb® G (80 to 100 mesh). The detection limits achieved for phosphorus and sulfur were at nanogram levels with the two columns.

The organic solvents used were found to suppress the $S_2$ and HPO emissions when co-eluted with the analyte; thus an efficient separation is necessary. A bluish emission appeared above the cavity where the organic solvent reached the cavity. Using an oxy-cavity while studying the separation of phosphorus and sulfur compounds in acetone or benzene, it was noticed that the $S_2$ emission was eliminated, while that of phosphorus at 526 nm was greater, probably due to the phosphorus continuum. Benzene and acetone gave measurable CH emissions ($\lambda_{max}$ = 431.5 nm), but the sensitivity was small because of great flame background and noise when using high amplification with the oxy-cavity.

The applicability of MECA for chromatographic detection was extended to silicon and nitrogen compounds. The conditions already established for the production of

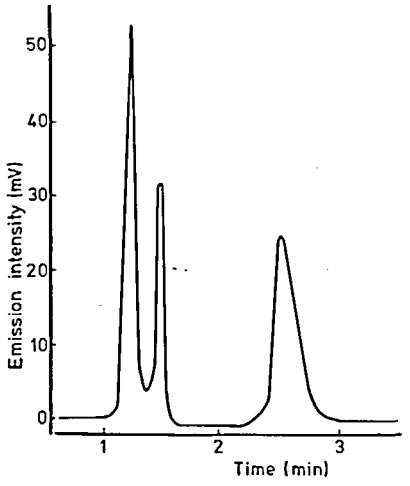



FIGURE 40. Separation of thionyl chloride (0.2 μg S), carbon disulfide (25 ng S), and 2-methyl thiophene (0.3 μg S) (in order of elution). Column temperature 180°C, 58 m*l* $N_2$ carrier $min^{-1}$, λ = 384 nm; slit = 0.2 mm (4 nm).



SiO emission were used, and the measurements were made at 580 nm to decrease the contribution from carbon and nitrogen species. Using the 10% SE-30 on Chromosorb® G column at 260°C, silicon compounds (*N*,O-bis[trimethylsilyl]acetamide [BSA], hexamethyldisilazane, phenyltrimethylsilane and *o*-tolyltrimethylsilane in acetonitrile) gave single peak responses.[41]

Silylation is a widely used reaction in gas chromatography to produce volatile products from hydrogen-bonded materials (e.g., carboxylic acids, alcohols, amines, and amides) and other nonvolatile compounds such as carbohydrates, peptides, and steroids. To establish the yields of conversion to the desired derivatives is a difficult task, including separation of derivatives by distillation, followed by elemental analysis. Not only has MECA been successfully used for monitoring SiO emissions from some silyl amino acid (methionine and aspartic acid) derivatives, but the MECA response can be used to indicate the type of derivative formed.[41]

The coefficient of variation for the determination of 5 μg of silicon as BSA using acetonitrile as solvent (six measurements by peak height) was 2% and the detection limit (1 μ*l* aliquots injected on to the column) was 0.1 μg of silicon. This is five times more sensitive than when used in conjunction with a volatilization system.

The white emission given by nitrogen compounds in an oxy-cavity was used to monitor primary and secondary amines at 500 nm after their separation by a chromatographic column. A detection limit of 1.2 μg of nitrogen as methylamine was achieved. $C_2$ emission is also monitored at 500 nm, and an increase in sensitivity was noticed for the same amount of nitrogen with an increasing number of carbon atoms in the amine molecule. As a result, a calibration graph might be constructed for each amine. However, if the contribution of carbon atoms is subtracted, only a single calibration graph is necessary for primary amines and another for second amines.

Most chromatographic studies described above used rather old modified flame emission spectrometers. The sensitivities achieved for all the compounds studied, although high, could be further improved by employing a specially built MECA detector. Chromatographic effluents containing halides, arsenic, antimony, tin, and boron also could

be monitored by the MECA detector with minor modifications. Research is also being carried out on adapting MECA for liquid chromatographic detection.[115]

## VII. CONCLUSION

MECA is a relatively simple, versatile, and rapid analytical technique with many advantages over established flame and related methods. It is mainly completementary to atomic spectrometry in that its greatest sensitivity is achieved for typical nonmetals such as sulfur, phosphorus, nitrogen, and the halogens. It is able to accommodate solid, liquid, or gaseous samples, often without further treatment, and has the almost unique ability among flame spectroscopic techniques of being able to speciate. Research is being conducted around the world, on expanding the scope of the technique, improving instrumentation, and establishing fields of application.

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