

**Photoacoustic spectroscopy applied to systems
involving photoinduced gas evolution or consumption**

Robert C. Gray, and Allen J. Bard

Anal. Chem., **1978**, 50 (9), 1262-1265 • DOI: 10.1021/ac50031a018 • Publication Date (Web): 01 May 2002

Downloaded from <http://pubs.acs.org> on February 16, 2009

More About This Article

The permalink <http://dx.doi.org/10.1021/ac50031a018> provides access to:

- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article



ACS Publications
High quality. High impact.

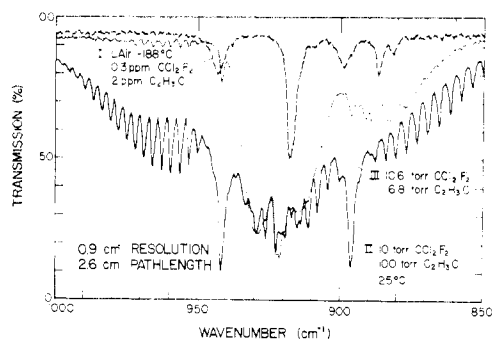


Figure 3. Infrared spectrum (curve I) of the mixture of CCl_2F_2 (0.3 ppm; features at 917.5 and 886.5 cm^{-1}) and $\text{C}_2\text{H}_3\text{Cl}$ (2 ppm; features at 943.0 and 899.0 cm^{-1}) dissolved in liquid air at -188°C , and spectra of 25°C mixtures of 10 Torr CCl_2F_2 and 100 Torr of $\text{C}_2\text{H}_3\text{Cl}$ (curve II) and 10.6 Torr of CCl_2F_2 and 6.8 Torr of $\text{C}_2\text{H}_3\text{Cl}$ (curve III)

with those for two gas-phase mixtures of the same compounds. It is apparent that little qualitative or quantitative information can be derived from the vapor phase spectra, whereas the bands of the solvated molecules are completely resolved.

One can test for saturated solutions by raising or lowering the temperature of the liquid and observing the effect on the absorption bands. The additive gases investigated are more soluble at higher temperatures. By maintaining a substantial pressure of solvent gas over the liquid, a broad liquid-phase temperature range is available for a given solvent.

Finally, the liquid-phase features are shifted in energy relative to the origins of vapor phase rotation-vibration bands. For example, gaseous CF_2Cl_2 has band origins at 922 and 882 cm^{-1} (3), whereas the observed transitions in solution are at 917.5 and 886.5 cm^{-1} , respectively. The magnitude of this shift is dependent on which solvent is used, but our data suggest that a more reasonable location for the quoted 882 cm^{-1} feature would be somewhat higher than 886.5 cm^{-1} .

CONCLUSIONS

We have demonstrated that conventional infrared spectrometry can be used to analyze trace impurities in some gases

with improved sensitivity if the mixture is liquefied. This work utilizes absorption pathlengths of the order of 1 cm, yet achieves sensitivities comparable to pathlengths of many meters under usual vapor-phase conditions. Increasing the effective pathlength by using a multiple traversal scheme or by actually lengthening the absorption cells would further improve the sensitivity of the method. The widths of the features observed in the cryogenic liquids are broader than the resolved rotational lines in low pressure gas-phase spectra but much narrower than those characteristic of high pressure.

Advantages of the technique then are (a) the high densities in the optical path and the higher peak absorption cross sections provide sensitivities which are greatly improved ($>10^3$) over atmospheric pressure gas-phase methodology for similar path lengths; (b) the higher densities of the trace impurities in the liquids mean that errors due to sorption or reaction at the walls of the spectroscopic cell are not as critical as in gases, where extremely small molar concentrations are typical for trace impurities; (c) once absorptivities are known at the liquid temperature, the method gives absolute concentrations independent of the pressure of the original gaseous sample; (d) chemical reactions of species which might be unstable in the gas phase may be suppressed at the very low temperatures used; and (e) the analysis of mixtures may be facilitated by the dramatic simplification of the absorption spectra.

ACKNOWLEDGMENT

The authors thank Bruce Stewart for his technical help and Jack P. Aldridge for his support of this work.

LITERATURE CITED

- (1) William B. Maier II, Samuel M. Freund, Redus F. Holland, and Willard H. Beattie, "Photolytic Separation of D from H in Cryogenic Solutions of Formaldehyde", submitted for publication in *J. Chem. Phys.*, 1978.
- (2) L. J. Marabella, *Appl. Spectrosc. Rev.*, **7**, 313 (1973).
- (3) "Tables of Molecular Vibrational Frequencies", T. Shimanouchi, Ed., *Phys. Chem. Ref. Data*, **3**, 269 (1974).

RECEIVED for review February 17, 1978. Accepted May 22, 1978. This work was performed under the auspices of the U.S. Department of Energy.

Photoacoustic Spectroscopy Applied to Systems Involving Photoinduced Gas Evolution or Consumption

Robert C. Gray and Allen J. Bard*

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

Photoacoustic spectroscopy (PAS) was used to study photoinduced reactions where PAS signals attributable to gas evolution and consumption have been observed in addition to the usual thermally generated pressure fluctuations. Examples of such PAS studies of oxygen consumption in the photooxidation of rubrene and gas evolution in the heterogeneous photocatalytic oxidation of acetic acid to methane and CO_2 at a platinumized TiO_2 catalyst are given. The sensitivity of the method and possible further applications are also described.

Recently there has been a resurgence of interest in the theory and applications of the photoacoustic effect and photoacoustic spectroscopy (PAS) (1-19). In the usual mode

of operation, PAS involves the detection (with a microphone) of a pressure wave induced by thermal changes in a sample upon absorption of light. The sample, enclosed in a leak-tight fixed volume cell, is illuminated with intensity modulated light. If some species in the sample absorbs the light and is promoted to an excited state, relaxation takes place, in part or totally, via radiationless transitions. These radiationless transitions generate heat which diffuses both into the sample and to the sample/gas interface. Heat transferred to the gas at this interface creates a pressure increase in a gas boundary layer at the sample surface which in turn compresses the remaining gas in the fixed volume cell. The amplitude of the pressure wave thus created depends on the incident light intensity, the modulation frequency, the relative thermal properties of the sample and gas, cell geometry, optical ab-

sorption coefficient of the sample species, the concentration of the absorbing species in the sample, and the quantum efficiency of the sample for radiative and nonradiative relaxation. Although a high quantum efficiency for radiative pathways leads to lower PAS signals, even in samples with luminescent efficiencies approaching unity a PAS signal may still be observed because of vibrational and solvent relaxation.

An alternate application of PAS, which has not to our knowledge previously been suggested, is to photochemical systems which involve the consumption or evolution of gases. In this case, pressure waves are generated directly by the modulated gas volume changes in addition to any photo-thermal pressure effects. There are a number of materials in which such effects might be observed, including those which undergo photoinduced reactions with oxygen, heterogeneous photocatalysts which induce gas phase or liquid phase reactions, and materials which show photoinduced adsorption or desorption of gases. In this paper we discuss this novel application of PAS and describe two experimental studies which illustrate this effect.

EXPERIMENTAL

Instrumentation. The spectrometer used in these studies is of the single beam variety similar to that previously described (13). The PAS signals detected by the lock-in amplifier, Princeton Applied Research (PAR) Model 186, were digitized and stored in a PAR Model 4101 scan recorder. All spectra were normalized to a carbon powder spectrum recorded under identical conditions and stored in the second channel of the scan recorder. No attempt was made to correct for lamp intensity fluctuations. Our studies indicated that short term lamp noise was primarily of a much higher frequency than the chopping rate and, therefore, was unimportant. Long term lamp drift amounted to no more than 0.5% per hour. Spectral noise was no more than $\pm 2\%$ of full scale for a carbon black signal. This noise was primarily due to quantizing errors in the analog-to-digital converter of the scan recorder and short term lamp fluctuations, these errors being amplified by the normalization process.

A new sample cell design was used with this system, which will be described in detail elsewhere (20). This cell provided for easier changing of samples and a smaller gas volume (0.2–0.25 cm³, depending on sample probe) and increased sensitivity compared to our previous one (13). The microphone used with this new cell was a B&K Model 4148 polarized by a highly stabilized 120-V power supply, yielding a sensitivity of 60 mV/Pa. The preamplifier used was identical with that of Munroe and Reichard (21).

Chemicals. Rubrene samples were prepared by dry mixing appropriate amounts of rubrene and magnesium oxide and adding a small amount of benzene to dissolve the rubrene. The resulting solution was either allowed to evaporate in air or the solvent was stripped in a Roto-vap to yield a dry powder of magnesium oxide uniformly coated with rubrene. These samples were prepared and stored until use in subdued light. The platinized TiO₂ was prepared by irradiation of a suspension of anatase in a solution of acetic acid and H₂PtCl₆ with a Hg-Xe lamp, as described in a recent communication (22). A weighed amount of the powder was introduced into the cell along with quantities of water and acetic acid measured with a microliter syringe.

RESULTS AND DISCUSSION

The thickness of the gas boundary layer (acoustic piston) (1, 2) formed by thermal diffusion in the gas, μ_g , is given by

$$\mu_g \cong (2\alpha_g/\omega)^{1/2} \quad (1)$$

where ω is the chopping frequency (rad/s) and α_g is the thermal diffusivity of the gas (cm²/s). For air at chopping frequency of 100 Hz, μ_g is about 0.2 cm. It is this boundary layer which is heated by thermal transfer from the sample surface and which in turn acts as a piston to compress the remaining gas in the cell. While the primary mechanism of motion of this boundary layer is heating and cooling through

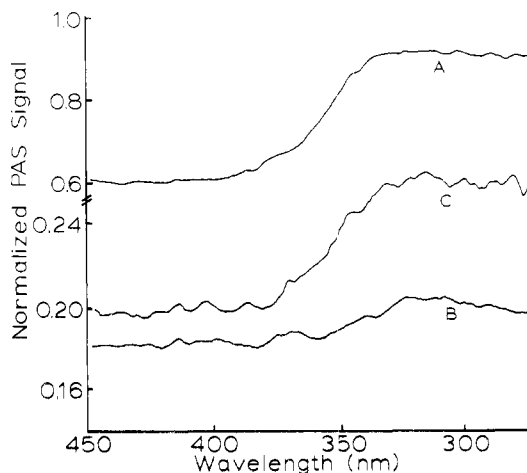
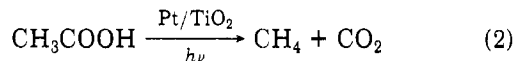


Figure 1. Effect of gas evolution on the PAS signals for platinized doped TiO₂ (anatase) in absence and presence of acetic acid. All spectra are normalized to carbon black. Experimental conditions: 6 nm resolution, 100 nm/min scan rate, 1-s time constant. (A) dry TiO₂ powder; (B) TiO₂ powder wet with benzonitrile; (C) sample in B with 10 μ L of acetic acid added

thermal transfer, any other perturbation which affects the pressure of this region will be reflected in the PAS signal. For example, if the sample upon illumination releases a gas, this gas will be added directly to the boundary layer increasing the pressure of the boundary layer above that for simple thermal transfer. The thermal transfer component of the PAS signal can and probably will still be present, however, and thus comparative studies will be necessary to determine the extent of signal enhancement by gas release. When a photoinitiated reaction consumes gas (e.g., O₂) from the boundary layer, the pressure in the boundary layer decreases. Again the boundary layer is still subject to thermal transfer from the sample. Thus, gas consumption may appear as a decrease in the normal PAS signal or even as a negative going signal, depending upon the relative rates of gas consumption and thermal transfer to the gas. Under conditions of coherent detection, phase shifts in the signal (with respect to a carbon black reference) can approach 180°.

Heterogeneous Photocatalytic Decomposition of Acetic Acid on Pt/TiO₂. In a recent report from this laboratory the decomposition of acetic acid containing suspended platinized anatase (Pt/TiO₂) powder under irradiation to form methane and CO₂ was described (22):



This reaction was chosen to illustrate the application of PAS to the study of heterogeneous photocatalysis. The usual PAS spectrum of the Pt/TiO₂ catalyst in the dry powdered form is shown in Figure 1A. The onset of light absorption occurs at 380 nm which corresponds to the known band gap energy (E_g) of anatase, 3.25 eV. When the sample is wet with benzonitrile, which does not undergo photodecomposition, the signal level is much smaller (Figure 1B), as is frequently observed with solid samples contacting liquids in PAS. However, when 10 μ L of glacial acetic acid are added to the sample, the signal level above E_g is clearly enhanced while the signal at longer wavelengths remains about the same. This clearly indicates an increase of the PAS signal due to gas release from the sample into the gas boundary layer. Similar experiments in which the catalyst was first wet with water, followed by addition of acetic acid have shown the same signal enhancement. The PAS study of heterogeneous photocatalysis clearly allows the action spectrum of the catalyst to be determined and should prove useful in determining the relative

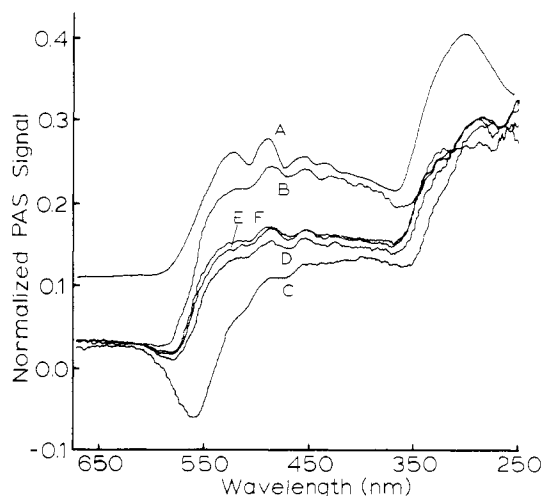
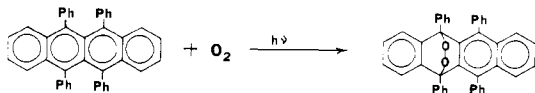


Figure 2. PAS of rubrene supported on MgO powder. Experimental conditions as in Figure 1. (A) reflectance spectrum of 5 wt % rubrene on MgO, dried in Roto-vap (ordinate in arbitrary units); (B) PAS spectrum of sample in A; (C) PAS spectrum of sample in B solvated with benzene, first scan; (D)–(F) are successive scans following C

efficiencies of different materials. A study of the PAS signal level as a function of chopping frequency should allow determination of the reaction rates. Studies of this type are currently under investigation.

Rubrene–Oxygen System. The photosensitized reaction of many aromatic hydrocarbons, such as rubrene (tetraphenylanthracene), with O_2 to form the endoperoxide has been widely studied [See (23–25) and references therein]. The reaction proceeds by the absorption of light by the rubrene, energy transfer to form singlet oxygen and attack of the singlet oxygen on the rubrene. The overall reaction is thus



Rubrene in solution shows absorption bands beginning at about 580 nm. Formation of the peroxide destroys the conjugation in one of the interior rings producing a pale yellow product whose absorption spectrum should be similar to that of 1,4-diphenylanthracene, with a broad featureless band centered at 300 nm. The PAS spectrum of a sample of 5 wt % rubrene on MgO dried in a Roto-vap is shown in Figure 2B. The PAS spectrum of this sample was close to that obtained by diffuse reflectance (Figure 2A) and was unchanged upon repeated scans. If the rubrene from this sample is redissolved in a small quantity of benzene which is allowed to evaporate in air to apparent dryness, enough benzene is retained on the sample to solvate the rubrene and, on exposure to light of wavelengths shorter than 580 nm in the presence of oxygen, the endoperoxidation reaction proceeds. The first scan from long wavelengths in taking the PAS spectrum of such a sample (Figure 2C) shows a large *negative* going transient due to oxygen uptake from the gas boundary layer which, in this case, is larger than the thermal diffusion signal at wavelengths at the foot of the absorption region. At shorter wavelengths, the absorbance increases and the negative O_2 -uptake signal is overtaken by the thermal signal. Figures 2, D–F are scans recorded immediately after 2C. Note that the initial negative-going signal is smaller on the second scan (D) and has disappeared by scan F. Note also the shoulder which grows in at 300 nm. This is the region where the photoproduct is expected to absorb. The final signal (F) looks much like the original one except for a diminished overall intensity in the rubrene band and the presence of a new band at 300 nm. This spectrum can be attributed to unreacted

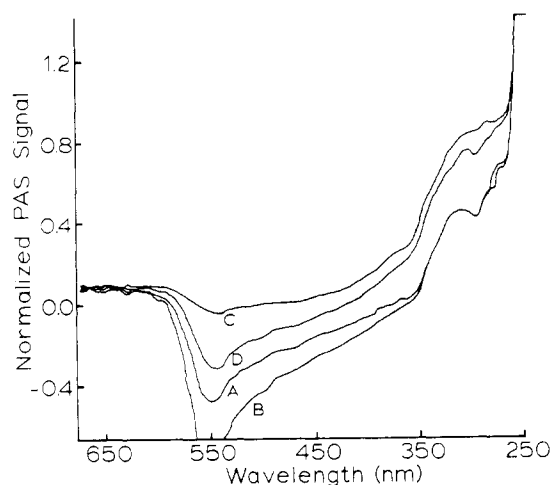


Figure 3. PAS of rubrene supported on MgO powder and dampened with benzene. Experimental conditions as in Figure 1. (A) first scan; (B) after sample in A allowed to stand in dark for 1 h; (C) after exposure of sample to full white light intensity of Xe lamp for 10 min; (D) after sample in C allowed to stand in dark for 15 min

rubrene lying under a layer of the photoproduct. PAS signals due to layers such as this one have been reported previously (18, 19). Physical examination of the sample after scan F reveals a yellowish band where the light had fallen. Slightly disturbing the sample surface with a spatula exposed a fresh surface and the same sequence of spectra (2C–F) were obtained: this process could be repeated until all of the powder surface area had reacted.

Since only the slightest trace of benzene solvent was present in the previous sample, diffusional mobility of the rubrene molecule was quite limited. A second, similarly prepared, sample was dampened with benzene to increase the mobility of rubrene. The spectra obtained for this sample are given in Figure 3. The signal in Figure 3A goes negative at the onset of rubrene absorption and remained negative until the onset of the photoproduct absorption band. The strong band in the UV end of the spectrum is due to the benzene absorption band at 260 nm. If the sample was then placed in the dark for 1 h, the spectrum in Figure 3B was obtained. The difference between A and B probably arises because the original sample was loaded in a room illuminated with fluorescent lamps, allowing partial reaction of the surface of the sample before A was run. On standing in the dark, the rubrene could reestablish a fresh homogeneous sample surface. Photolysis of the sample in the full white light intensity of the lamp for 10 min gave rise to spectrum C. In this spectrum, the exposed sample area has been almost totally reacted, as evidenced by the absence of an absorption band by rubrene and the presence of a strong photoproduct band. After this sample stood in the dark for 15 min, spectrum D was obtained. Either unreacted rubrene had diffused into the illuminated area and some of the photoproducts had diffused out or decomposition of the endoperoxide occurred. This would produce an increased negative-going signal at the rubrene wavelengths and a decreased signal at the photoproducts wavelength. Photolysis for a sufficiently long time eventually removed all signals at the rubrene wavelengths leaving only the photoproduct band. Note that this negative-going PAS signal and the observed time dependent behavior were unique to rubrene. Samples of other materials which do not react with oxygen (e.g. anthracene or 9,10-dibromoanthracene) do not show such a response.

Photoinitiated reactions with oxygen (or other gases) are important in several areas, such as the photodegradation of polymers, pharmaceuticals, and foods. PAS measurements could play a useful role in the study of such reactions.

CONCLUSIONS

These examples demonstrate the utility of PAS in the study of photochemical reactions involving gas evolution and consumption. An estimate of the sensitivity of the technique can be obtained by assuming a sinusoidal wave form and a minimum detectable signal level of 1% of that of carbon black powder.

The sensitivity of the microphone is 6 mV/ μ bar; the cell volume, 0.25 cm³; and the average signal level found for carbon black powder was 1 mV. This signal level corresponds to an rms pressure change of 0.17 μ bar. Assuming an ideal gas, we find this is equivalent to a gas volume change of 4.2×10^{-8} cm³ rms (or 1.2×10^{-7} cm³ peak to peak). Thus, detection at 1% represents 1.2×10^{-9} cm³ (p-p) and at STP this corresponds to 5.3×10^{-14} mol of gas consumed or released per cycle. The average scan time of a PAS spectrum was 200 s, so that at 60-Hz modulation frequency, a maximum of 6.3×10^{-11} mol of gas need be produced or consumed to be detectable in an entire scan. Even if signal levels approaching that of carbon are required, the total amount of gas is only 6.3×10^{-9} mol. Clearly PAS is quite a sensitive technique for studying these types of reactions. Note also that the above calculation assumes irradiation with monochromatic light of rather low intensity (about 1 mW/cm²). Much larger signals could be obtained using laser excitation or the full output of the xenon lamp. Cells could easily be constructed as well to measure photoeffects directly by sunlight.

While the technique can be used for comparative measurement and for obtaining action spectra for photochemical reactions, careful calibration and a suitable theoretical model may allow the use of PAS in quantitative studies as well. We must stress that this is only a preliminary study and the method requires further investigation. However, the basic concepts described here appear correct and these early

successes are quite encouraging.

ACKNOWLEDGMENT

We are indebted to Bernhard Kraeutler for the sample of Pt/TiO₂ and to Michael E. Long for obtaining the reflectance spectrum of rubrene-MgO.

LITERATURE CITED

- (1) A. Rosencwaig and A. Gersho, *Science*, **190**, 557 (1975).
- (2) A. Rosencwaig and A. Gersho, *J. Appl. Phys.*, **47**, 64 (1976).
- (3) A. Fromowitz, P.-S. Yeh, and S. Yee, *J. Appl. Phys.*, **48**, 209 (1977).
- (4) H. S. Bennett and R. A. Forman, *Appl. Opt.*, **15**, 1313 (1976).
- (5) H. S. Bennett and N. A. Forman, *Appl. Opt.*, **15**, 2405 (1976).
- (6) H. S. Bennett and R. A. Forman, *J. Appl. Phys.*, **48**, 1432 (1977).
- (7) J. G. Parker, *Appl. Opt.*, **12**, 2974 (1973).
- (8) L. C. Aamodt, J. C. Murphy, and J. G. Parker, *J. Appl. Phys.*, **48**, 927 (1977).
- (9) J. C. Murphy and L. C. Aamodt, *J. Appl. Phys.*, **48**, 3502 (1977).
- (10) A. Rosencwaig, *Anal. Chem.*, **47**, 592A (1975).
- (11) W. R. Harshbarger and M. B. Robin, *Acc. Chem. Res.*, **6**, 329 (1973).
- (12) M. J. Adams, B. C. Beadle, A. A. King, and G. F. Kirkbright, *Analyst (London)*, **101**, 553 (1976).
- (13) R. C. Gray, V. A. Fishman, and A. J. Bard, *Anal. Chem.*, **49**, 697 (1977).
- (14) J. B. Callis, *J. Res. Nat. Bur. Stand., Sect. A*, **80**, 413 (1976).
- (15) W. Lahmann and H. J. Ludewig, *Chem. Phys. Lett.*, **45**, 177 (1977).
- (16) M. J. Adams, J. G. Highfield, and G. F. Kirkbright, *Anal. Chem.*, **49**, 1850 (1977).
- (17) J. A. Burt, *Anal. Chem.*, **49**, 1130 (1977).
- (18) M. J. Adams, and G. F. Kirkbright, *Analyst (London)*, **102**, 281 (1977).
- (19) M. J. Adams, and G. F. Kirkbright, *Spectrosc. Lett.*, **9**, 255 (1976).
- (20) R. C. Gray and A. J. Bard, manuscript in preparation.
- (21) D. M. Munroe and H. S. Reichard, Princeton Applied Research, *Appl. Note*, **147**.
- (22) B. Kraeutler and A. J. Bard, *J. Am. Chem. Soc.*, **100**, 2239 (1978); **99**, 7729 (1977).
- (23) K. Gollnick, in "Advances in Photochemistry", W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Ed., Vol. 6, Interscience, New York, N.Y., 1968.
- (24) B. Munroe, *J. Phys. Chem.*, **81**, 1861 (1977).
- (25) B. Stevens and J. A. Ors, *J. Phys. Chem.*, **80**, 2164 (1976).

RECEIVED for review March 9, 1978. Accepted May 15, 1978. The support of this research by the National Science Foundation is gratefully acknowledged.

X-ray Microanalysis of a Natural Mordenite-Containing Rock and Its Ion-Exchanged Derivatives

János Papp,* Erzsébet Czárán, and András Jánossy¹

Central Research Institute for Chemistry of the Hungarian Academy of Sciences, P.O. Box 17, 1525 Budapest, Hungary

The chemical composition of a natural mordenite and its ion-exchanged derivatives was determined by x-ray microanalysis. In the analysis, crystal particles smaller than 0.5 μ m were used, which are thin enough to make ZAF correction unnecessary. Sufficiently accurate quantitative results can be obtained by the revised methods of Russ and of Hall, or by the combination of the two. Interaction with various agents leads to different extents of ion exchange, while treatment with hydrochloric acid leads to a partial dealumination, as well.

Natural zeolites of practical significance are found generally as sedimentary rock which contains other crystalline and amorphous materials as well. The determination of the

chemical composition of the zeolite phase is largely impeded since the zeolite phase cannot be separated from the secondary minerals by simple means. Yet the proper knowledge of the chemical composition of the zeolite and its modified, e.g. ion-exchanged, form is essential when using them as catalysts or adsorbents.

There is a convenient method which allows direct chemical analysis without separation: x-ray microanalysis (1). In the present paper, we describe our analytical results obtained on the crystalline phase of a natural mordenite mineral of Hungarian origin.

Single mordenite crystals are usually much smaller than the x-ray spatial resolution (governed mainly by electron spreading in the sample) on thick materials, so the conventional microprobe approach had to be rejected. Instead, we analyzed single crystals on carbon-coated electron microscopic grids in the transmission mode where the analyzed thickness was below 0.5 μ m. Efforts were made to analyze

¹ Institute of Biophysics, Biological Research Centre, Hungarian Academy of Sciences, P.O. Box 521, 6701 Szeged, Hungary.