at 0°C]; about 1.4 × $10^6$ tons of ethylene (obtained by cracking the ethane product); and 2.7 × $10^6$ tons of benzene. These are, respectively, 1, 13, and 50 percent of the 1973 U.S. consumption.

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13. In most of the Bureau's experiments at short gas residence times, coal catalyzed with 1 percent molybdenum was treated at 400 atm at 800°C. Hiteshue *et al.* (*5*) reported a 26 percent yield (by weight of coal) at 6 seconds and a 4.5 percent yield of a lighter liquid at 30 seconds. Friedman *et al.* (*2*) reported liquid yields of 35, 41, 31, 23, and 10 percent at 2.3, 5, 6.7, 10, and 25 seconds, respectively. The yield of single-ring aromatics at 5, 6.7, and 25 seconds was 3.4, 4.1, and 3.5 percent, respectively. The yield of asphaltenes at 6.7 seconds was 3.7 percent, and the liquid produced at 2.3 seconds was heavier than that at 5 seconds. These liquids from rapid heating were far heavier than the liquids from flash heating reported here.
14. R. A. Graff, S. Dobner, and A. M. Squires (in preparation) give further experimental details and results of an exploration of coal heating rate, time of the coal sample at the reaction temperature, gas environment, and vapor residence time.
15. The Illinois State Geological Survey supplied the coal sample and its ultimate analysis (percent by weight, moisture-free basis) was as follows: hydrogen, 5.11; carbon, 68.18; nitrogen, 1.06; oxygen, 9.38; sulfur, 4.16; and ash, 12.11.
16. S. Dobner, R. A. Graff, and A. M. Squires (in preparation) give detailed results on which Figs. 2 and 3 are based.
17. The work is supported by grant AER-72-03426 A No. 4 (formerly GI-34286) from the RANN Program (Research Applied to National Needs) of the National Science Foundation. Under this grant, we are also studying high-velocity fluidized beds suitable for flash-hydrogenating coal. We thank A. Chiaravalotti, who performed most of the experiments; E. Gilbert, who assisted in developing the experiment; and R. D. Harvey and his colleagues at the Illinois State Geological Survey for their cooperation.

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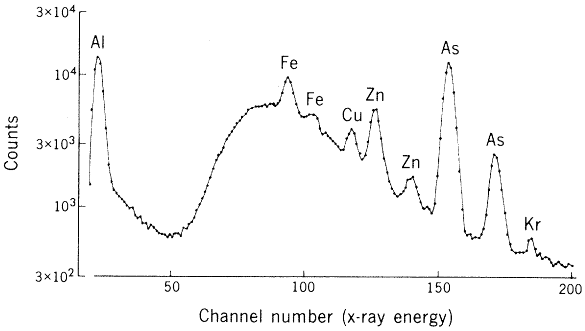
# Scanning Proton-Induced X-ray Microspectrometry in an Atmospheric Environment

Abstract. *Collimated million-electron-volt proton beams, brought out into air, can be used as a scanning microprobe to examine specimens with a spatial resolution of the order of 1 micrometer. Trace elements at concentrations as low as 1 part per million can be detected. Some preliminary results based on the use of this simple method are presented.*

X-ray emission spectroscopy, induced either by incident x-rays of higher energy (fluorescence) or by bombardment with charged particles, has been used as a tool for the detection of extremely small quantities (as little as $10^{-12}$ g) of particular chemical elements (*1–3*). Protons of energies ≈ 2 to 4 Mev are particularly effective, combining large x-ray production cross sections with small x-ray backgrounds [the dominant x-ray background coming from proton bremsstrahlung and secondary-electron bremsstrahlung (*4*)]; indeed, the method is so sensitive to trace concentrations that the difficulty of preparing sufficiently pure substrate materials often poses a practical limitation (*2*). Roughly speaking, concentrations of the order of 1 part in $10^6$ or $10^7$ are detectable in reasonably short times, as compared with limiting concentrations of 1 part in $10^2$ for (continuum) x-ray–induced fluorescence and 1 part in $10^3$ for the electron microprobe (*4, 5*).

Unlike neutron activation, x-ray emission is immediate, and so it is possible to use a scanning point source to produce x-ray emission pictures or micrographs. This has been done with electrons [the "scanning electron microprobe" (*6*)], with x-rays [both conventional x-ray sources (*7*) and collimated synchrotron radiation (*8*) have

Fig. 1. X-ray energy spectrum from a silicon wafer doped with 60 ppm of arsenic. The aluminum x-rays are produced by fluorescence from silicon x-rays in an aluminum foil covering the detector; atmospheric krypton, as well as metallic impurities, are also clearly visible.



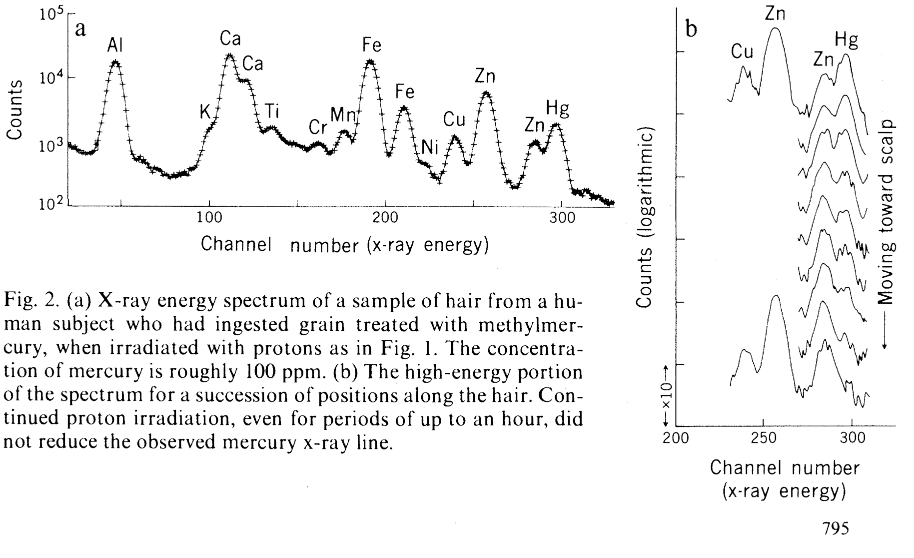


Fig. 2. (a) X-ray energy spectrum of a sample of hair from a human subject who had ingested grain treated with methylmercury, when irradiated with protons as in Fig. 1. The concentration of mercury is roughly 100 ppm. (b) The high-energy portion of the spectrum for a succession of positions along the hair. Continued proton irradiation, even for periods of up to an hour, did not reduce the observed mercury x-ray line.

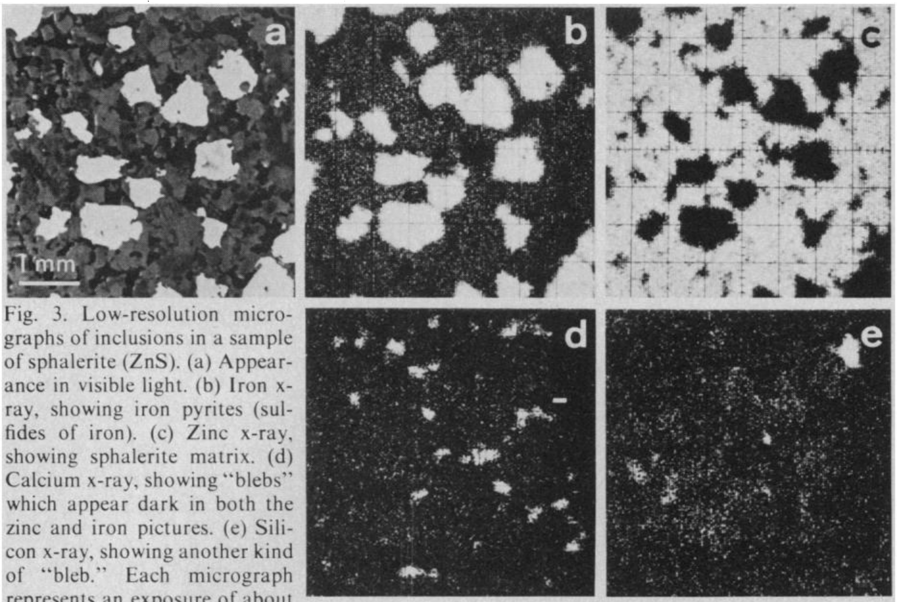


Fig. 3. Low-resolution micrographs of inclusions in a sample of sphalerite (ZnS). (a) Appearance in visible light. (b) Iron x-ray, showing iron pyrites (sulfides of iron). (c) Zinc x-ray, showing sphalerite matrix. (d) Calcium x-ray, showing "blebs" which appear dark in both the zinc and iron pictures. (e) Silicon x-ray, showing another kind of "bleb." Each micrograph represents an exposure of about 5 minutes and has a spatial resolution of about 150 μm (determined by the pinhole diameter).

been used], and, most recently, with an electromagnetically focused proton beam (*9*).

With the exception of x-ray–induced fluorescence, the above techniques have been carried out in vacuo. For specimens of biological interest and for general convenience, it would be highly desirable to operate in an atmospheric environment. Can this be done with protons? We have investigated this problem and find no fundamental difficulties. The simplest technique would be to collimate an emergent proton beam by means of a pinhole; the resultant pencil beam strikes a sample, scanned mechanically in a raster pattern in a plane perpendicular to the beam. X-ray emission as a function of time (not position), as detected by energy-dispersive detectors [Si(Li), for example], is used to construct a picture of the distribution of each chemical element, most simply by intensifying the trace of an oscilloscope whose *X* and *Y* deflections follow the sample's motion. [This is very similar to the technique used in (*8*), where a schematic diagram and further detail may be found.]

For proton energies of 2 to 4 Mev, optimum for trace element detection (*4*), protons emerge easily through thin windows and have ranges of about 100 μm in biological tissues (which allows sections as thick as ≈ 10 μm to be examined). Pinholes fabricated in metals 50 to 100 μm thick form completely effective collimators, and reasonable air or helium paths contribute negligible attenuation to both proton beam and emitted x-rays. Expected count rates, for realistic proton beam intensities, allow detection of concentrations between 1 part in 10$^4$ and 1 part in 10$^6$ over spatial distributions of several micrometers in size (*10*). The most serious problem is multiple scattering of the collimated proton beam, both in the sample and in the air path from pinhole to sample. Calculations of this effect indicate that, for specimens much thinner than 100 μm, resolution approaching 1 μm is attainable (*11*). Pinholes of this size have been fabricated (*8*) and would pass sufficient beam current, given a realistic incident proton intensity (100 μa/mm$^2$). Thus element-discriminating micrographs can be made of specimens up to ≈ 10 μm thick, with the entire thickness imaged in focus at 1-μm resolution. Furthermore, the depth of field at this resolution is enormous by the standards of ordinary microscopy—roughly 1000 μm. Resolution significantly higher than 1 μm would require operation in vacuo, electromagnetic focusing methods, and much thinner specimen sections.

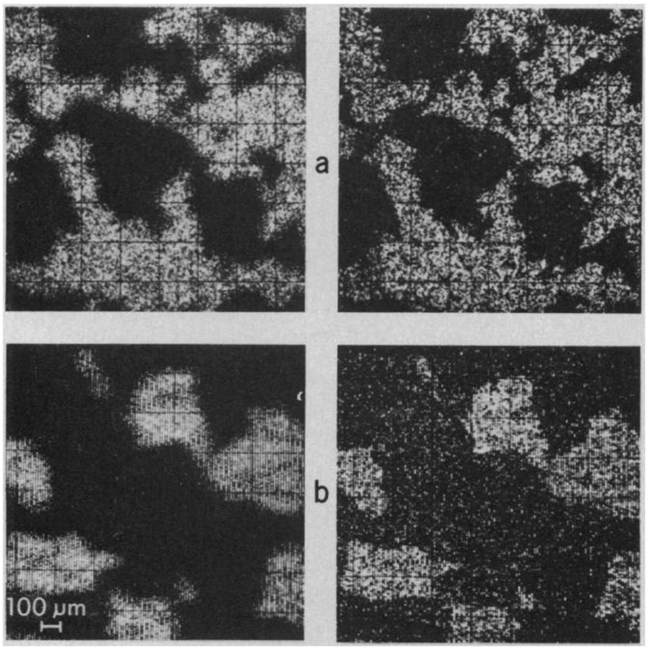


Fig. 4. Comparison micrographs of the sphalerite sample, at higher magnification, showing the improvement obtained with the use of a 25-μm pinhole (right) compared with the larger pinhole (left) as used in Fig. 3. (a) Zinc x-ray. (b) Iron x-ray.

We have carried out some preliminary experiments with an emergent proton beam from the Lincoln Laboratory Van de Graaff accelerator. Figure 1 shows an x-ray spectrum obtained, after 10 minutes of counting, from a silicon wafer doped with 60 parts per million (ppm) of arsenic and bombarded with 100 na of 2-Mev protons in a helium environment; from the observed arsenic K x-ray peak, one can calculate that an arsenic concentration of 1 part in 10$^7$ would be detectable under the same conditions, yielding a peak 5 standard deviations above background. A similar undoped silicon wafer showed no arsenic peak whatsoever. This observed sensitivity is close to the theoretical limit for detectability in vacuo (*4*); in other words, no sensitivity is lost by operating in a helium atmosphere.

An interesting application of this technique is to examine human hair, making a one-dimensional scan along the fiber, in order to map out the chronology of heavy-metal poisoning, for example. Figure 2 shows the result of an analysis of a sample of hair obtained from an Iraqi who had ingested seed grain treated with methylmercury (as a fungicide). The whole spectrum (Fig. 2a) shows many lines, including a strong mercury line and a nearby zinc line. The high-energy portion of the spectrum (Fig. 2b) is shown for points progressively closer to the scalp; comparison with the zinc line, presumably constant in intensity, shows monotonically decreasing amounts of mercury since the last haircut (in agreement with chemical analysis of the same specimen), before which ingestion took place. The specimen was in a helium atmosphere for these spectra.

Figure 3a shows a geochemical application—a two-dimensional scan of a piece of sphalerite (ZnS) containing inclusions of iron pyrites (sulfides of iron). An *XY* stage driven by a stepping motor moved the sample in a raster pattern past the stationary pinhole. The iron picture (Fig. 3b) and zinc picture (Fig. 3c) account for most of the specimen, but occasional dark spots in *both* aroused our curiosity; spectra at those points identified two different kinds of "blebs," one rich in calcium (Fig. 3d) and the other rich in silicon (Fig. 3e). These pictures were taken in air, which has the additional advantages of preventing sample charging, owing to the ionized discharge path along the proton beam, as well as of allowing cooling of the sample by convection from the surface. [Air has the disadvantage of showing a strong argon line, and, at a much lower level, a krypton line (1.1 ppm in air). The ability to see these natural constituents gives some idea of the sensitivity of this technique. A helium environment eliminates these lines, of course, and, in addition, reduces multiple scattering and attenuation.]

The results so far have been obtained with a crude experimental arrangement—a low beam current (1 to 100 pa), large pinholes, and a small detector. Some idea of the improvement possible with smaller pinholes is shown in Fig. 4, the sphalerite specimen at higher magnification. The smaller pinhole (25 μm in diameter) yields considerably better resolution, at the expense of signal. By using a smaller pinhole, some electromagnetic prefocusing, higher beam intensities, along with computerized data-taking and the techniques of image enhancement, we expect to improve the microscope's capabilities, reaching a resolution of $\lesssim 1$ μm.

Owing to its properties of (i) operation in an atmospheric environment, (ii) relatively high penetrating power, and (iii) chemical element discrimination, even of adjacent elements in the periodic table at extremely low concentrations, the scanning proton microprobe would appear to have applications in many disciplines but most particularly in the biological sciences. Microscopy of hydrated or even live specimens is possible; alternatively, the specimen could be frozen or maintained in an atmosphere saturated with water vapor to prevent drying of thin specimens during exposure. Very little preparation is needed—it is not necessary to stain the specimen or to produce thin sections—and, because of the good penetration, with consequent large depth of field, it is possible to make in-focus micrographs of the same object viewed at two angles, with subsequent stereoscopic interpretation. The range of possible applications, several of which are now being pursued, includes environmental studies (distribution of contaminants in microorganisms); human biochemical assays (for example, in hair) in subjects both living and dead (mummies); solid-state studies (junctions, microcrystals, and the like); cell biology; and metallurgy. The availability of about 100 proton accelerators in this country alone, capable of producing 2- to 4-Mev beams of sufficient intensity ($\gtrsim 10$ μa/mm$^2$), should make this extremely simple technique attractive for research in a variety of disciplines.

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10. For instance, 1 na of 2-Mev protons incident on a carbon matrix (1 mg/cm$^2$) containing 1 part in $10^4$ by weight of a trace element produces count rates (in counts per second) of $3 \times 10^3$, $6 \times 10^2$, $1.5 \times 10^2$, $9 \times 10^2$, and $7.5 \times 10^2$ for trace elements of atomic number 12 (magnesium), 20 (calcium), 30 (zinc), 40 (zirconium), and 50 (tin), respectively, assuming a detector subtending $0.1 \times 4\pi$ steradian.
11. For instance, multiple scattering of the collimated proton beam in air, from pinhole to sample, broadens the beam by about 0.2 μm for 2-Mev protons over a path length of 0.1 mm; for a path length of 1 mm the broadening is 5.8 μm. The corresponding figures for a helium path are 0.04 and 1.4 μm. Multiple scattering in the target sample broadens a 2-Mev proton beam by 0.18 μm for a 1 mg/cm$^2$ carbon sample of unit density (10 μm in thickness); for a 10 mg/cm$^2$ sample (100 μm in thickness) the corresponding figure is 5.8 μm.
12. We thank J. Ryan and H. Rosen (Lincoln Laboratory, Massachusetts Institute of Technology) for their proton beam and laboratory support, W. Ladd and A. Eisenman for assistance in construction and data-taking, M. Bottino (Brooklyn College) who provided the sphalerite sample, and T. Clarkson (University of Rochester) who provided the hair sample. This work was supported with funds from the Alfred P. Sloan Foundation, the National Science Foundation (grant DMA 74-23522), and the Atomic Energy Commission [contract At(11-1)-3069].

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# Hydroxyl Radical Concentrations Measured in Ambient Air

*Abstract.* *Diurnal variations in the hydroxyl radical concentration of ambient air were measured for the first time by the technique of laser-induced fluorescence.*

It has been suggested in recent years that the hydroxyl radical (HO) is a major driving force in the chemistry of the atmosphere. It sustains photochemical chain reactions which determine the chemical transformation of numerous trace constituents of urban (*1*) and natural atmospheres (*2*). A measurement of the HO concentration in the atmosphere could provide a vital new insight into the understanding of photochemical smog as well as a better quantitative basis for the assessment of the impact of man-made chemical emissions on a global scale.

The HO concentration has been estimated from considerations of the global balance of CO (*3*) and from photochemical considerations of reactions operative in the troposphere (*4*). It has been measured in the stratosphere by observing the fluorescence of HO excited by the solar radiation (*5*). However, this technique cannot be used for HO measurements at lower altitudes because of the reduced fluorescence efficiency and the multitude of interferences present there. Very recently, a measurement of HO concentration at ground level has been made by means of laser-induced fluorescence (*6*). We report here on the HO concentration in the open air measured by means of this technique.

*Detection scheme.* The technique of laser-induced fluorescence for HO measurements involves the excitation of HO radicals from the ground electronic state to the first excited electronic state and the detection of the resulting fluorescence emitted by the excited HO. At ambient temperatures, most of the population resides in the lowest two rotational levels of the ground state. The excitation used in this work was the $P_1(2)$ line near 2825.8 Å in the $^2\Pi(\nu = 0) \rightarrow {}^2\Sigma^+(\nu = 1)$ transitions (*7, 8*) of HO. The excited HO undergoes very fast relaxation under atmospheric conditions, finds its way into the $^2\Sigma^+(\nu = 0)$ manifold, and then fluoresces in the $^2\Sigma^+(\nu = 0) \rightarrow {}^2\Pi(\nu = 0)$ transitions (*6, 8*). This fluorescence is centered around 3090 Å, with a spectral width of about 30 Å. The HO concentration is then deduced from the fluorescence measurements by the use of Eq. 1:

$$n = S(A\sigma_a\eta_F)^{-1} \qquad (1)$$

Here $n$ represents the HO concentration in the focal region of excitation; $S$ is the fluorescence signal; $A$ is a measure of the intensity of excitation and the detection efficiency for the particular arrangement em-