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# ELECTRON SPECTROSCOPE ANALYSIS OF THE ATOMIC CONTENT OF SAMPLES OF OCCUPATIONAL HEALTH INTEREST

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# SUMMARY

A total of 25 samples were received and examined by induced electron emission spectroscopy (also known as ESCA). Included were dried lung tissue from miners, coal dusts from Pennsylvania and Utah, different minerals containing $SiO_2$, a cement powder, and porous filters which had been used to trap dust particles. Elemental identification and estimated weight percentages were determined for these samples.

Measurements of the binding energies of the Si(2p) and Si(2s) levels of the $SiO_2$-containing minerals were made to see if there were significant binding energy differences between these minerals. No experimentally significant differences were observed.

A tabulation of detection limits for our current spectrometer for 33 elements was prepared. These limits were determined for a specific set of operating conditions and can be reduced by employing longer total scan times.

Specific problems concerned with induced electron emission spectroscopy are discussed. Some suggested applications to work of potential interest to health and environmental studies are outlined. Comments are given on instrumental improvements available to improve the quality of induced electron emission spectral results and to reduce the time required for analyses.

## TABLE OF CONTENTS

# LIST OF TABLES

# I. INTRODUCTION

The purpose of the work supported by Contract No. HSM-099-71-54 was to evaluate the usefulness of induced electron emission spectroscopy (IEE), also known as ESCA, or electron spectroscopy for chemical analysis, to problems typical of those handled by the National Institute of Occupational Safety and Health. The evaluation was to be based on the results obtained by IEE on a maximum of forty samples prepared and supplied by the National Institute of Occupational Safety and Health, Cincinnati, Ohio.

An induced electron emission spectrometer measures the binding energies of the inner shell electrons of all elements except hydrogen. A sample is irradiated with soft X-rays, typically the $K\alpha_{1,2}$ lines of aluminum which have an energy of 1486 electron volts. The absorption of these X-rays by elements in a sample causes photoelectrons to be ejected. The kinetic energy of an ejected photoelectron is equal to the difference between the X-ray energy and the binding energy of the ejected electron in its element. A measurement of the kinetic energy of the ejected electron, with a suitable correction for work function, allows the binding energy of that particular photoelectron to be determined. The number of photoelectrons produced per second under fixed spectrometer conditions is a function of the amount of that element in a thin section of the sample surface.

An IEE spectrometer is capable of observing only those elements that are within 50 to 100 Å of the surface. This limitation results not from a limit in X-ray penetration depth, but from the fact that the photoelectrons observed as a spectral line must leave the sample without losing energy through a collision. Photoelectrons produced at depths of the order of 100 Å and greater have a high probability of suffering a collision which results in a loss of energy.

Results have been obtained on 25 samples submitted and are discussed below. In addition, the results of particular experiments with some of these samples, and results from some experiments of our own are included. These additional results and data are used as examples in the discussion of particular characteristics of IEE spectral data.

## II. EXPERIMENTAL PROCEDURE

A Varian Associates model IEE-15 induced electron emission spectrometer was used to obtain all experimental results. The X-ray source is a circular aluminum anode which was operated at an anode potential of 10 KV and an anode current of 60 ma. A 4K Varian 620i computer was used with the standard Varian 4K IEE program to control spectrometer parameters and collect spectral data.

Several spectrometer modifications were supplied by Varian and installed in the spectrometer during the period of this contract. Of these, the one of major importance to the results was the installation of a thinner shield between the X-ray region and the sample. This resulted in an increase in X-ray flux to the sample and a resulting increase by a factor of 1.6 in observed counts per second for a given sample. A correction has been applied to the few early samples run before this change was made.

All samples were prepared for the spectrometer by placing them on 1/2 inch wide double sticky Scotch® tape which had previously been placed around the circumference of a standard aluminum sample slug. A standard sample slug is 3/4 inch long by 7/16 inch in diameter; a hole is drilled through the center with a number 1 drill for mounting on the sample probe.

Samples on circular filters supplied to us were first cut into a 3/4 inch wide strip and then applied to the double sticky Scotch® tape surface on the sample holder. No difficulty was experienced in handling them in this manner.

Wide scans were run on all samples except for the samples of crystalline forms of silica. The wide scans for all elements covered the binding energy range of 0 to 1100 electron volts. Since the spectrometer can scan only a 100 volt segment at a time, eleven 100 volt segments were scanned to cover the desired range. Each segment was scanned 50 successive times at a rate of 10 seconds per scan. The number of channels used per each segment was reduced from the value of 200 stated in our proposal to 100. This was done to reduce the number of computer instruction changes required during a wide scan. It also has the desirable effect of doubling the observation time for each point of data obtained and thus improves the signal-to-noise ratio without increasing the total scanning time. Under these conditions the spectrometer accumulates information for a total of 5.0 seconds for each of the 100 channels.

Narrow scans of 20 electron volt widths were run at a scan time of 10 seconds and 50 scans were accumulated in 100 channels. Under these conditions, the total time the spectrometer scans a particular channel is the same as that of the wide scan. However, the real spectral peaks are better defined and permit a more accurate measurement of binding energies.

In the qualitative interpretation of wide scan spectra, we quickly found that the attempted identification of all lines which were twice the noise level, as suggested in our proposal, made the interpretation of spectra difficult and very time-consuming. The real problem is that maximum noise signals can easily become as great as twice the average noise as averaged by eye. Some judgment was used in selecting lines, and possibly some elements of low concentration have been missed.

The work with wide scan spectra also pointed out the need for a large reference collection of experimental binding energies and relative intensities for essentially all elements. We had prepared a tabulation by binding energy of all levels of all elements in the range of 10 to 1100 ev from Siegbahn's data. Although very useful, the data in the tabulation do not always agree with values observed on our spectrometer. For an element such as nitrogen a range of binding energies from approximately 395 ev to 410 ev is more appropriate than the single value of 399 ev from Siegbahn's table.

Two sources of lines other than direct photoelectron levels are (1) satellite lines from the $AlK\alpha_{3,4}$ X-ray line of the source and (2) Auger lines. The satellite lines appear because the X-ray source produces its principal radiation of $AlK\alpha_{1,2}$ at 1486 ev and a secondary radiation, the $AlK\alpha_{3,4}$, of approximately one tenth the intensity of the primary radiation at an energy of 1496 ev. Thus, all intense photoelectron lines will be accompanied by a less intense line (0.075 times the main line intensity) at a binding energy 10 volts lower in energy.

The Auger lines are produced through internal conversion of energy within an atom which has already lost a photoelectron. The vacancy left by the emitted photoelectron is filled by a higher level electron in the atom. As this electron drops to the vacancy it loses energy either through the emission of an X-ray (X-ray fluorescence) or through the ejection of another electron from the atom. Such an electron is an Auger electron. The Auger levels that we have observed have all been much less intense and usually broader than the primary photoelectron. An exception to this is the Auger line of sodium at a binding energy of 498 ev which is relatively intense and sharp. However, the sharp Auger lines can easily be identified by the <u>absence</u> of a satellite line 10 volts lower in binding energy. The satellite line is missing because the kinetic energy of the Auger electron is independent of the source of the original vacancy in the atom.

Quantitative estimates were based on measured counts per second. A more detailed discussion of quantitative analytical work was included as Appendix A of Dow Proposal No. 571865.

## III. RESULTS

### A. SAMPLE LISTING AND ELEMENTAL SENSITIVITY DATA

Induced electron emission spectra and analytical results have been obtained for the 26 samples submitted. For reference purposes, the sample numbers and sample descriptions are tabulated in Table I.

Table II gives sensitivity data for 33 elements. Among these are the more commonly found elements and include a good range of sensitivities. The estimated detection limits are based on the assumption that a line of 25 counts per second can be observed above the noise. Admittedly, this may be somewhat optimistic for some elements. We must also assume that a narrow scan of 20 volts width is run for at least 50 scans at a scan time of 10 seconds with 100 channels for data storage. The sensitivity can be increased by increasing the observation time. Signal-to-noise increases as the square root of the observation time.

Two entries are given for copper in Table II. The sensitivity for a metallic copper surface is much greater than that observed for copper in a compound. In fact, the copper count rate for a really clean copper surface is probably considerably higher than the value shown in the table. We have no explanation for these observations.

The sensitivity given for iron, Fe, should be considered as only a very rough estimate. In the spectral region used to observe iron, two normal lines occur at approximately 715 and 729 ev. However, for some iron samples these lines become

## Table I

## Description of Samples Received

| | |
|---|---|
| 1000 | Cement-Allentown Portland Type I #65-CS-4 |
| 1001 | Coal Miners' Lung #48208 Low Temp. Ash |
| 1002 | Utah Coal Dust (Bulk) |
| 1003 | Pennsylvania Coal Dust 1 (Bulk) |
| 1004 | Pennsylvania Coal Dust 2 (Bulk) |
| 1005 | Utah Coal Dust on Filter 101-2.16 mg |
| 1006 | Utah Coal Dust on Filter 119-1.09 mg |
| 1007 | Utah Coal Dust on Filter 126-0.61 mg |
| 1008 | Pennsylvania Coal Dust on Filter 131-1.65 mg |
| 1009 | Pennsylvania Coal Dust on Filter 105-1.02 mg |
| 1010 | Pennsylvania Coal Dust on Filter 117-0.89 mg |
| 1011 | Tridymite-Synthetic from Quartz |
| 1012 | Cristobalite-Synthetic $SiO_2$ |
| 1013 | Kaolin |
| 1014 | Quartz <10 μ |
| 1015 | Crysatile-Johns Manville 4D (Bulk) |
| 1016 | Crysatile-Johns Manville 4D (Ground at $LN_2$ temp.) |
| 1017 | Filter 13-Possible Alumina, Silica, Carbon, Iron Oxide-0.64 mg |
| 1018 | Filter 18-Asbestos-0.58 mg |
| 1019 | Filter 22-Bronze smelting fume-0.36 mg |
| 1020 | Filter X-2 - Detergent Dust -11.84 mg |
| 1021 | Filter 2-Foundry Dust-1.64 mg |
| 1022 | Filter 7-Welding Fume-3.18 mg |
| 1023 | LTA Ash of Coal Miners' Lung #48206-75.2 mg |
| 1024 | LTA Ash of Coal Miners' Lung #48115-64.9 mg |
| 1025* | Blank Millipore Filters |

*These numbers were arbitrarily assigned here for record keeping purposes only.

## Table II

## Estimated Sensitivities of Selected Elements

| Element | Source | Observed Counts/sec 10KV-60 ma | Counts/sec for 100 wt,% of Element | Estimated Detection Limit wt,% |
|---|---|---|---|---|
| Ag | Silver | 3,110 | 3,110 | 0.8 |
| Al | Aluminum | 1,460 | 1,460 | 2.0 |
| As | $As_2O_3$ | 1,480 | 1,950 | 1.3 |
| Ba | $Ba(NO_3)_2$ | 4,690 | 8,950 | 0.3 |
| B | BN | 2,240 | 5,140 | 0.5 |
| Bi | $Bi_2O_3$ | 7,230 | 8,060 | 0.3 |
| Br | KBr | 1,400 | 2,080 | 1.2 |
| Ca | $CaF_2$ | 6,210 | 12,110 | 0.2 |
| C | $C_6H_5Cl$ | 6,570 | 10,270 | 0.2 |
| Ce | $CeF_3$ | 2,520 | 3,540 | 0.7 |
| Cl | $C_6H_5Cl$ | 2,190 | 6,950 | 0.4 |
| Co | CoO | 4,270 | 5,432 | 0.5 |
| Cr | $K_2Cr_2O_7$ | 2,110 | 5,960 | 0.4 |
| Cu | Copper | 31,690 | 31,690 | 0.08 |
| Cu | CuO | 3,960 | 4,960 | 0.5 |
| F | Teflon® $(CF_3)_n$ | 42,500 | 55,920 | 0.04 |
| Fe | $FeF_3$ | 420 | 850 | 2.9 |
| Hg | $HgI_2$ | 2,320 | 5,255 | 0.5 |
| I | NaI | 10,000 | 11,800 | 0.2 |
| K | KCl | 3,450 | 6,580 | 0.4 |
| Mg | $MgF_2$ | 520 | 1,350 | 1.9 |
| Mn | $MnO_2$ | 3,150 | 4,980 | 0.5 |
| N | $NaNO_2$ | 1,680 | 8,320 | 0.3 |
| Na | NaCl | 9,200 | 23,360 | 0.1 |
| O | $NaNO_3$ | 6,330 | 11,210 | 0.2 |
| P | $P_2O_5$ | 1,160 | 2,650 | 0.9 |
| Pb | Lead | 9,420 | 9,420 | 0.3 |

### Table II

### Estimated Sensitivities of Selected Elements (Continued)

| Element | Source | Observed Counts/sec 10KV-60 ma | Counts/sec for 100 wt,% of Element | Estimated Detection Limit wt,% |
|---|---|---|---|---|
| Pr | $PrCl_3$ | 3,660 | 6,421 | 0.4 |
| Pt | Platinum | 3,740 | 3,740 | 0.7 |
| S | ZnS | 1,614 | 4,905 | 0.5 |
| Se | $WSe_2$ | 2,720 | 5,900 | 0.4 |
| Si | $SiO_2$ | 931 | 1,994 | 1.2 |
| Sn | 50-50 Solder | 6,120 | 12,240 | 0.2 |
| Ti | $TiO_2$ | 6,600 | 11,000 | 0.2 |
| V | $VO_2$ | 3,540 | 5,770 | 0.4 |
| W | $WSe_2$ | 2,270 | 4,220 | 0.6 |
| Zn | ZnS | 12,790 | 19,060 | 0.1 |

very broad and are just barely distinguishable as separate peaks. For a relatively clean iron surface, the width of the lines decrease. The detection limit for iron becomes dependent on the state of the iron.

As part of our contract we were requested to provide information on times required to obtain an analysis. The following are good approximations for our present procedures and equipment:

| | |
|---|---|
| Sample preparation and introduction | 10 minutes |
| Spectrometer scanning time-wide scan | 130 minutes |
| Plotting time and computer output time | 35 minutes |
| Time to setup spectrometer and rescan a single peak over 20 volt range | 15 minutes/peak |
| Analysis time (varies widely with sample) | 60 minutes |

With the newest Varian IEE spectrometer, all scanning times are reduced by a factor of about 10. Rescanning of individual lines is not required; any desired portion of a wide scan can be expanded, displayed and plotted.

## B. SPECTROMETER REPRODUCIBILITY

An induced electron emission spectrometer provides two types of information, binding energies for qualitative identification, and photoelectron counts per second for quantitative determinations. An evaluation of a particular spectrometer should include a measure of how well the spectrometer will reproduce these two quantities. To truly evaluate the spectrometer, sample preparation problems must be eliminated as much as possible. We have chosen cylinders of Teflon®, machined to clean the surface before analysis, as a standard sample to check our spectrometer.

Table III gives the binding energy measurements for carbon and fluorine obtained for a number of standard Teflon® runs. Also included are the observed net counts per second (maximum counts per second - minimum counts per second) for carbon and fluorine. The maximum spread of binding energies for both carbon and fluorine is 0.6 ev. Measured binding energy shifts for carbon and fluorine were in the same direction and by the same amount, within experimental error, for scans made on a particular day. We now believe that the range of binding energies measured was in part, at least, the result of drift in the retarding potential power supply. Varian discovered that some drift did occur, and very recently have sent us instructions for wiring changes which eliminate the drift problem by keeping this power supply energized all of the time the spectrometer is on - not just during spectral scans. We

## Table III

## Measured Binding Energies of Card F in Teflon® as a Function of Time

| Date | Carbon |  | Fluorine |  |
|---|---|---|---|---|
|  | Binding Energy(ev) | Net Counts/sec | Binding Energy(ev) | Net Counts/sec |
| Jan 27, 1972 | 294.7 | 5,010 | 691.4 | 35,860 |
| *Feb 10, 1972 | 294.8 | 5,400 | 691.5 | 39,990 |
| Feb 14, 1972 | 294.8 | 5,600 | 691.4 | 41,170 |
| Feb 15, 1972 | 295.1 | 5,520 | 691.8 | 40,790 |
| Feb 16, 1972 | 294.9 | 5,590 | 691.6 | 41,840 |
| Feb 17, 1972 | 295.1 | 5,420 | 691.8 | 41,080 |
| Feb 25, 1972 | 294.9 | 5,760 | 691.5 | 43,190 |
| Mar 18, 1972 | 294.7 | 5,460 | 691.4 | 42,870 |
| Mar 29, 1972 | 294.5 | 5,000 | 691.2 | 42,500 |

*Pulse amplifier trigger was reset on Feb 4, 1972. This resulted in an increase in counts per second observed.

do not as yet have adequate data to verify that our measured binding energies are more constant with this change incorporated.

The counts per second for carbon and fluorine given in Table III are typical of sensitivity variations observed at that time. No attempt was made to optimize the reproducibility of the spectrometer. Reproducibility for the same sample for runs made during a day are better. Table IV gives the maximum, minimum, and net counts per second observed for five successive runs within one hour of the zinc region of sample no. 1022. The maximum spread is 530 counts per second, or 2.1% of the largest net count. These scans were plotted and are shown in Figure 1. The agreement between the binding energies of the peaks is quite good.

Table IV

Repeated Scans of Zn from Sample No. 1022

| Run Number | Maximum Counts/sec | Minimum Counts/sec | Net Counts/sec |
|---|---|---|---|
| 1 | 37,948 | 13,630 | 24,318 |
| 2 | 38,280 | 13,574 | 24,706 |
| 3 | 38,244 | 13,748 | 24,496 |
| 4 | 38,148 | 13,568 | 24,580 |
| 5 | 37,632 | 13,456 | 24,176 |

## C. BINDING ENERGIES OF SILICON IN FORMS OF $SiO_2$

In discussions concerning this contract, the question of determining different forms of $SiO_2$ from binding energy differences was raised. To investigate this question samples 1011 through 1016 were scanned along with an API standard

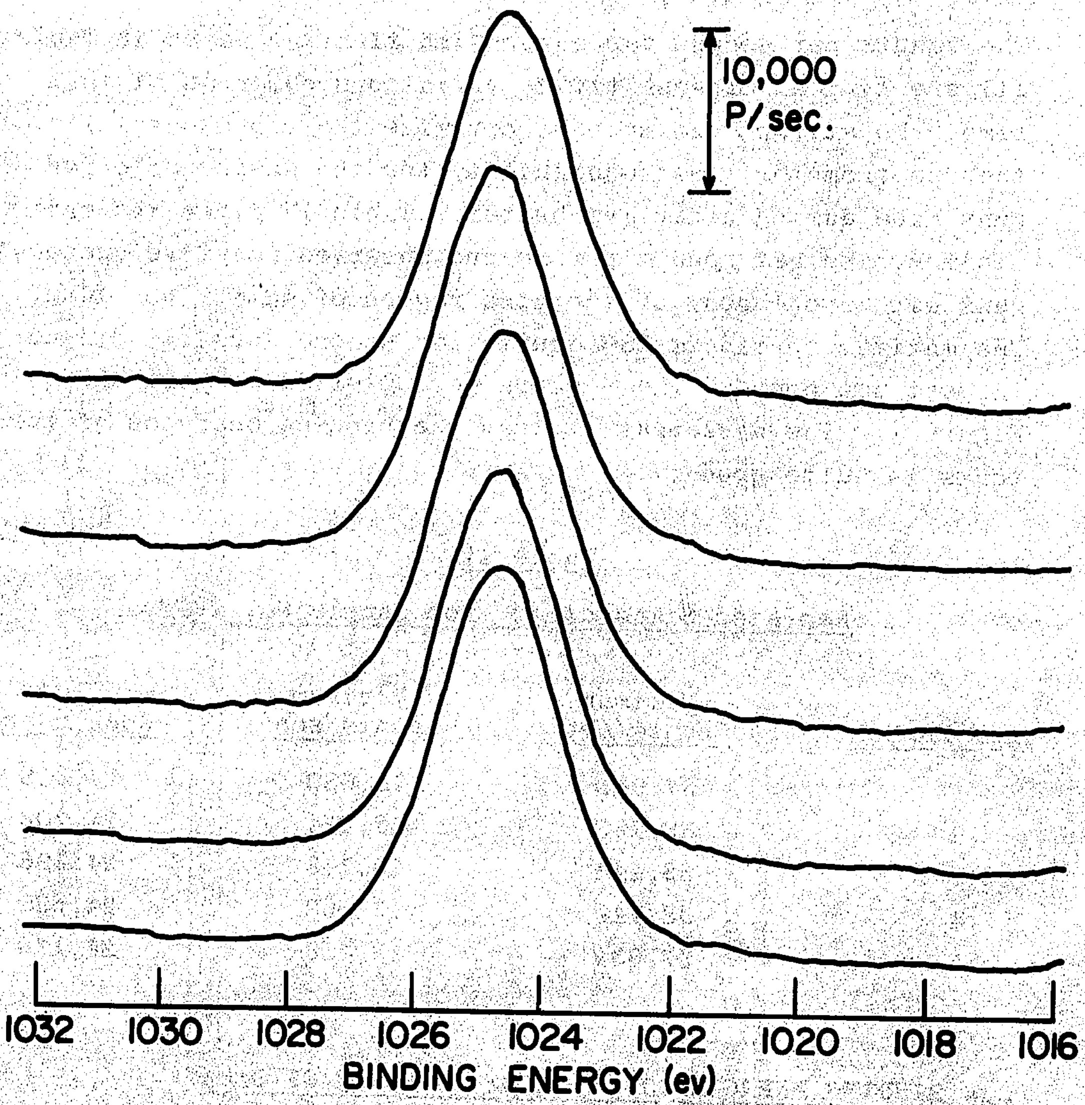
10,000
P/sec.
1032
1030
1028
1026
1024
1022
1020
1018
1016
BINDING ENERGY (ev)

Fig. 1

kaolinite from the Dixie Rubber Pit at Bath, South Carolina. These data are given in Table V. Data are entered as two numbers: the upper underlined number is the observed binding energy in electron volts, while the number immediately below is the net counts per second for the observed line. Samples 1011 through 1014 show no large change in the binding energies of either the Si(2p) or the Si(2s) levels.

The silicon results for samples 1015, 1016 and the API standard kaolinite appear to be substantially different. However, if a correction for change in sample surface charge effect is applied using 286.3 ev as a reference carbon binding energy, then the Si(2p) results for samples 1011 through 1016 and API kaolinite becomes:

| | |
|---|---|
| 1011 | Si(2p) = 104.7 ev |
| 1012 | 105.1 ev |
| 1013 | 104.5 ev |
| 1014 | 104.7 ev |
| 1015 | 104.5 ev |
| 1016 | 104.6 ev |
| Kaolinite | 104.0 ev |

Although the Si(2p) binding energy for kaolinite is lower than the other values by more than expected experimental accuracy, additional work would be required to prove that this difference is real. The value of 105.1 ev for 1012, Cristobalite also appears to be higher than the other results. Again, extensive tests would be required to prove that this difference is real and useful in an analytical procedure. As expected, the API standard kaolinite showed a good aluminum line.

Table VI gives data obtained for silicon in blends with sample number 1003, Penna. coal dust No. 1. A small but significant

## Table V

## Spectral Data for a Series of Silicates

| Sample No. | Description | Silicon<br>Si(2s) | Silicon<br>Si(2p) | Oxygen | Carbon |
|---|---|---|---|---|---|
| 1011 | Tridymite-Synthetic from Quartz | 155.7 ev<br>1,240 | 104.6 ev<br>1,550 | 533.9 ev<br>10,210 | 286.2 ev<br>984 |
| 1012 | Cristobalite-Synthetic $SiO_2$ | 155.6 ev<br>1,000 | 104.8 ev<br>1,250 | 533.7 ev<br>8,080 | 286.0 ev<br>840 |
| 1013 | Kaolin | 155.4 ev<br>770 | 104.5 ev<br>870 | 533.5 ev<br>10,780 | 286.3 ev<br>1,190 |
| 1014 | Quartz <10 µ | 155.5 ev<br>1,420 | 104.5 ev<br>1,680 | 533.6 ev<br>10,980 | 286.1 ev<br>1,450 |
| 1015 | Chrysatile-John Manville 4D (Bulk) | | 105.0 ev<br>720 | 533.6 ev<br>9,280 | 286.8 ev<br>430 |
| 1016 | Chrysatile-John Manville-ground at $LN_2$ temp. | | 106.1 ev<br>883 | 534.4 ev<br>11,750 | 287.8 ev<br>560 |
| | Kaolinite-API Std. | Al-76.6 ev<br>580 | 105.0 ev<br>900 | 534.1 ev<br>13,060 | 287.3 ev<br>1,050 |

## Table VI

## Si(2p) Binding Energies in Blends with Coal

| | Silicon | | | |
|---|---|---|---|---|
| Sample Description | Si(2p) | Calculated Wt,% Si | Oxygen | Carbon |
| 1003-Penna Coal Dust #1[a] | 100.8 ev<br>62 | 3 wt,% | 530.7 ev<br>1,510 | 282.4 ev<br>4,650 |
| 9.9 wt,% Cristobalite (1012) in Penna Coal Dust (1003) | 101.5 ev<br>163 | 8 wt,% | | |
| 10.1 wt,% Kaolinite (API Std) in Penna Coal Dust (1003) | 102.6 ev<br>336 | 17 wt,% | | |
| 50.0 wt,% Kaolinite (API Std) in Penna Coal Dust (1003) | 104.6 ev<br>1,010 | 51 wt,% | | |

[a] 180 scans were run on silicon to improve the signal-to-noise. The peak noise in the silicon spectrum was about 10 counts/second. 90 scans were run on the three blends.

line was observed at a binding energy of 100.8 ev for the Si(2p) level in the coal sample. If the carbon line is again used as a reference to correct for surface change effect, as above, then the corrected Si(2p) binding energy becomes 100.8 + 3.9 = 104.7 ev, in reasonable agreement with the Si(2p) binding energies reported for samples 1011 through 1014. Note that in this run of 180 scans, the minimum detectable peak is certainly lower than the 25 counts per second used to calculate the data of Table II.

The three blends reported in Table VI were designed to show the effects of mixing materials of different electrical conductivity. Spectra of the silicon region of sample no. 1003, Penna coal dust, the blend of 9.9 wt % cristobalite in Penna coal and the blend of 10.1 wt % kaolinite (API) in Penna coal are shown as A, B, and C, respectively, in Figure 2. These runs were made from new samples after the basic data runs reported in Table VI, and may differ somewhat. The decrease of the binding energy of Si(2p) with increasing concentrations of the coal dust probably results from increasing conductivity of the mixtures with a resulting decrease in surface charge. We have observed similar results in mixtures of inorganic salts with graphite. These data illustrate the need for a reliable internal standard when determining accurate binding energies. Unfortunately, oxygen and carbon scans were not run on these mixtures.

The quantitative results for the blends illustrate some of the problems peculiar to quantitative determinations by IEE. The actual weight percentage of Si in kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) is 26.7 wt %. From one of our scans of the Si(2p) line in kaolinite, we observed a line of 1260 counts per second, or 63.2 wt % based on our calibration run on $SiO_2$ as quartz. If the spectrometer is giving valid data, then this result tells

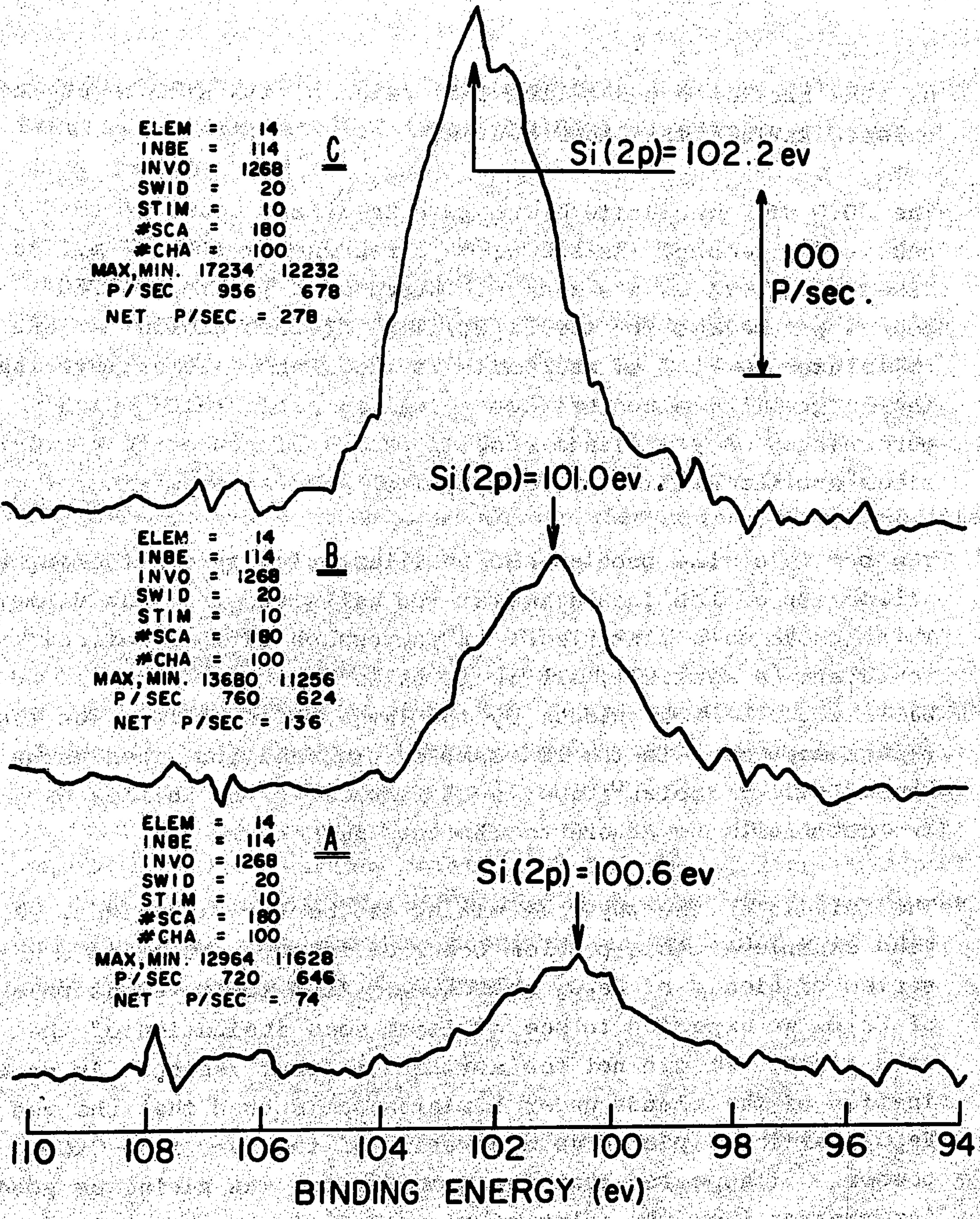
ELEM = 14
INBE = 114
INVO = 1268
SWID = 20
STIM = 10
#SCA = 180
#CHA = 100
MAX,MIN. 17234 12232
P/SEC 956 678
NET P/SEC = 278
C
Si(2p)= 102.2 ev
100 P/sec.
Si(2p)=101.0 ev
ELEM = 14
INBE = 114
INVO = 1268
SWID = 20
STIM = 10
#SCA = 180
#CHA = 100
MAX,MIN. 13680 11256
P/SEC 760 624
NET P/SEC = 136
B
ELEM = 14
INBE = 114
INVO = 1268
SWID = 20
STIM = 10
#SCA = 180
#CHA = 100
MAX,MIN. 12964 11628
P/SEC 720 646
NET P/SEC = 74
A
Si(2p)=100.6 ev
110
108
106
104
102
100
98
96
94
BINDING ENERGY (ev)

FIG. 2

us that kaolinite has a larger fraction of its silicon on the exposed surface than does quartz.

The 50.0 wt % kaolinite blend gave an Si(2p) count of 1010 counts per second. As shown, this represents 51 wt % silicon based on quartz as a standard. Based on a figure of 1260 counts per second for the Si(2p) line of pure kaolinite, one calculates 80 wt % of kaolinite in the blend. We believe that the large differences between actual and calculated weight percentages of the blends results from differences in particle sizes and the details of the physical process of mixing.

The particle size problem can be illustrated by considering a collection of 1/8 inch diameter red balls and 1/2 inch diameter white balls on a flat plane. A photograph of this collection would show essentially all white balls because the small red balls would be well hidden by the large white balls. The same phenomena occurs in the IEE sample. In addition, when using double sticky Scotch® tape, a difference in the ability of two components to adhere to the tape may occur.

The details of the physical mixing can be very important. A good example of this problem occurred in our results on a series of blends of $Fe_2O_3$ and $CaCO_3$. At 5 to 10 weight percent of $Fe_2O_3$ we expected to see at least some indication of the iron lines. We did not see anything in that region. An examination of the blends under a microscope showed that the red $Fe_2O_3$ particles picked up a covering of the very fine $CaCO_3$ powder. It appeared that the spectrometer was giving us good information from the point-of-view of surface composition.

## D. COLLECTED RESULTS ON SUBMITTED SAMPLES

The samples submitted consisted of 12 powdered samples which included 3 samples of miners' lungs and 12 samples of dust collected on filters plus unexposed blanks of the filters. Results for samples 1011 through 1016 inclusive were given above in Table III.

The remaining data were separated into separate tables according to the nature of the samples. Table VII contains the results on the three lung samples, Table VIII gives the results for coal and cement dusts, while Table IX gives the results for dust samples collected on Filters. Figure 3 shows scans of the 900 to 1000, and 1000 to 1100 ev regions of sample no. 1022 of filter 7 with welding fumes. These are typical of the 100 volt segments used to obtain wide scans of the submitted samples.

As expected, the filter blank (several were actually run with identical results) contained carbon and oxygen. The appearance of the nitrogen line at about 407 ev was unexpected. A nitrogen at this binding energy is most probably from an $NO_3$ group, but some organic $-NO_2$ groups cannot be ruled out. Since this line is from the filter paper it serves as a rough indicator of the degree of filter surface coverage by the dust. A heavy deposit of dust would completely cover the surface of the filter paper and no 407 ev peak would be observed (unless, of course, the dust itself contained $NO_3$ groups).

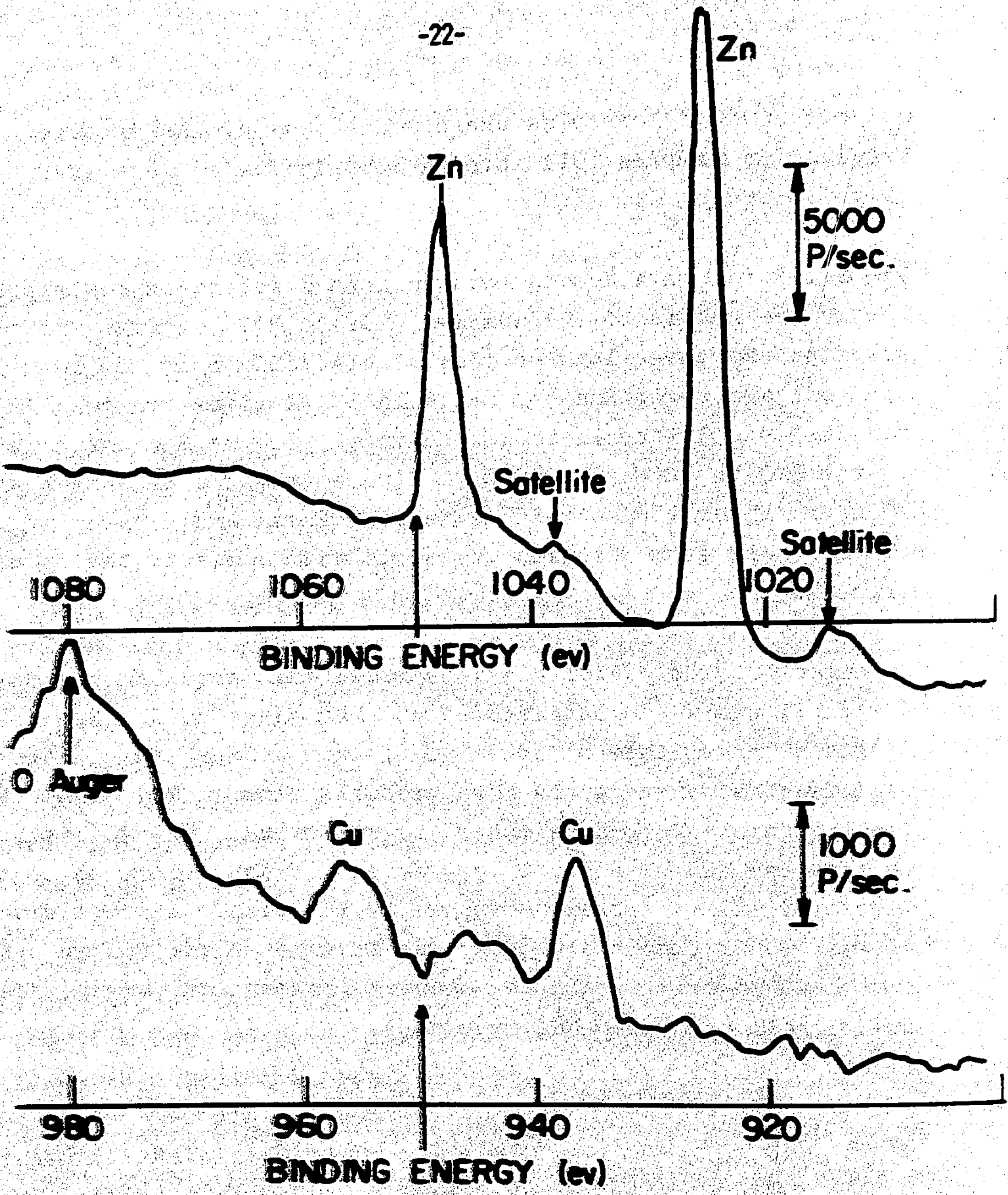
Zn
Zn
5000 P/sec.
Satellite
Satellite
1080
1060
1040
1020
BINDING ENERGY (ev)
O Auger
Cu
Cu
1000 P/sec.
980
960
940
920
BINDING ENERGY (ev)

Fig. 3

## Table VII

## Data From Lung Samples

### Sample #1001-Low Temperature Ashed Coal Miners' Lung #48208

| Binding Energy(ev) | Element | Peak Intensity (c/sec) | Estimated wt,% |
|---|---|---|---|
| 101.9 | Si | 124 | 6 |
| 133.1 | P | 390 | 15 |
| 168.6 | S(sulfate) | 250 | 5 |
| 285.2 | C | 1790 | 17 |
| 400.2 | N(amine) | 350 | 4 |
| 532.0 | O | 6420 | 57 |
| 1071.9 | Na | 1920 | 8 |

### Sample #1023-Lung #48206, 0.0752 g LTA Ash

| Binding Energy(ev) | Element | Peak Intensity (c/sec) | Estimated wt,% |
|---|---|---|---|
| 103.7 | Si | 110 | 6 |
| 134.6 | P | 169 | 6 |
| 169.5 | S(sulfate) | 144 | 2.9 |
| 286.0 | C | 818 | 8 |
| 401.0 | N(amine) | 132 | 1.6 |
| 532.3 | O | 3290 | 29 |
| 714.2 | Fe? | 80 | 9 |
| 1072.0 | Na | 1180 | 5.1 |

### Sample #1024-Lung #48115, 0.0649 g LTA Ash

| Binding Energy(ev) | Element | Peak Intensity (c/sec) | Estimated wt,% |
|---|---|---|---|
| 102.1 | Si | 65 | 3 |
| 134.3 | P | 100 | 4 |
| 169.0 | S(sulfate) | 71 | 1.4 |
| 285.1 | C | 1080 | 11 |
| 532.0 | O | 2090 | 19 |
| 1071.8 | Na | 870 | 3.7 |

## Table VIII

## Data From Coal and Cement Samples

| Binding Energy(ev) | Element | Peak Intensity (c/sec) | Estimated wt.% |
|---|---|---|---|
| **Sample #1000-Allentown Portland Cement Type I** | | | |
| 102.6 | Si | 96 | 5 |
| 286.2 | C | 670 | 7 |
| 533.0 | O | 2570 | 23 |
| | No Cr observed | | |
| **Sample #1002-Utah Coal Dust (Bulk)** | | | |
| 101.0 | Si | 40 | 2 |
| 282.6 | C | 2560 | 25 |
| 398 broad | N(amine + ring) | 140 | 1.7 |
| 530.8 | O | 1210 | 11 |
| **Sample #1003-Penna Coal Dust, 1 (Bulk)** | | | |
| 100.8 | Si | 39 | 2 |
| 282.4 | C | 2910 | 28 |
| 397 broad | N(ring) | 140 | 1.7 |
| 530.7 | O | 940 | 8 |
| **Sample #1004-Penna Coal Dust, 2 (Bulk)** | | | |
| 100.2 | Si | 51 | 3 |
| 166.7 | S(sulfide?) | 57 | 1.2 |
| 282.3 | C | 4140 | 40 |
| 398 | N | 95 | 1.1 |
| 530.5 | O | 1190 | 11 |

## Table IX

## Data From Dust on Filters

| Binding Energy(ev) | Element | Peak Intensity (c/sec) | Estimated wt.% |
|---|---|---|---|
| **Sample #1005-Utah Coal Dust on Filter 101-2.16 mg** | | | |
| 101.0 | Si | 50 | 2.5 |
| 283.1 | C | 4500 | 44 |
| 397.8 | N(amine or ring) | 127 | 1.5 |
| 531.0 | O | 2350 | 21 |
| 1071.9 | Na | 74 | 0.3 |
| Possibility of small trace of zinc | | | |
| **Sample #1006-Utah Coal Dust on Filter 119-1.09 mg** | | | |
| 283.9 | C | 2720 | 26 |
| 407.0 | N(nitrate) | 370 | 4.4 |
| 532.5 | O | 2640 | 24 |
| 1070.8 | Na | 20 | 0.09 |
| **Sample #1007-Utah Coal Dust on Filter 126-0.61 mg** | | | |
| 101.8 | Si | 30 | 1.5 |
| 284.3 | C | 3140 | 31 |
| 398.1 | N(ring) | 90 | 1.1 |
| 406.9 | N(nitrate) | 550 | 7 |
| 532.3 | O | 3780 | 34 |
| **Sample #1008-Penna Coal Dust on Filter 131-1.65 mg** | | | |
| 99.8 | Si | 92 | 4.6 |
| 281.7 | C | 3600 | 35 |
| 406.1 | N(nitrate) | 104 | 1.3 |
| 529.8 | O | 1540 | 14 |

## Table IX

## Data From Dust on Filters (Continued)

| Binding Energy(ev) | Element | Peak Intensity (c/sec) | Estimated wt,% |
|---|---|---|---|
| **Sample #1009-Penna Coal Dust on Filter 105-1.02 mg** | | | |
| 101.5 | Si | 47 | 2 |
| 283.0 | C | 4590 | 45 |
| 407.0 | N(nitrate) | 224 | 2.7 |
| 532.0 | O | 2090 | 19 |
| 1027.8 | Zn? | 58 | 0.3 |
| **Sample #1010-Penna Coal Dust on Filter 117-0.89 mg** | | | |
| 283.0 | C | 3750 | 37 |
| 406.8 | N(nitrate) | 400 | 4.8 |
| 532.5 | O | 3130 | 28 |
| **Sample #1017-Filter 13-Possible, Alumina, Silica, Carbon, Iron Oxide 0.64 mg** | | | |
| 102 | Si | 74 | 4 |
| 285.5 | C | 1660 | 16 |
| 407.2 | N(nitrate) | 630 | 7.6 |
| 532.8 | O | 4590 | 41 |
| 1071.5 | Na | 120 | 0.5 |
| **Sample #1018-Filter 18-Asbestos-0.58 mg** | | | |
| 50.0 | Mg | 47 | 3 |
| 103.1 | Si | 58 | 3 |
| 142.9 | Pb | 35 | 0.4 |
| 169.0 | S(sulfate) | 48 | 1.0 |
| 286.9 | C | 2140 | 21 |
| 407.1 | N(nitrate) | 950 | 11 |
| 529.9 | O | 6500 | 58 |
| 1072.1 | Na | 120 | 0.5 |

## Table IX

## Data From Dust on Filters (Continued)

**Sample #1019-Filter 22-Bronze Smelting Fume-0.36 mg**

| Binding Energy(ev) | Element | Peak Intensity (c/sec) | Estimated wt,% |
|---|---|---|---|
| 286.0 | C | 2220 | 22 |
| 407.0 | N(nitrate) | 740 | 9 |
| 533.0 | O | 5530 | 49 |
| 1021.8 | Zn | 160 | 0.8 |
| 1071.7 | Na | 400 | 1.7 |
| **Sample #1020-Filter X-2-Detergent Dust-11.84 mg** | | | |
| 133.0 | P | 75 | 3 |
| 168.5 | S(Sulfate) | 278 | 6 |
| 198.8 | $Cl(Cl^-)$ | 20 | 0.3 |
| 232.0 | Ta? | 133 | No std. available |
| 284.8 | C | 2090 | 20 |
| 531.5 | O | 2230 | 20 |
| 1071.5 | Na | 2700 | 12 |
| **Sample #1021-Filter 2-Foundry Dust-1.64 mg** | | | |
| 103.0 | Si | 130 | 7 |
| 286.3 | C | 1730 | 17 |
| 407.0 | N(nitrate) | 740 | 9 |
| 532.8 | O | 5380 | 48 |
| 1071.3 | Na | 180 | 0.8 |
| **Sample #1022-Filter 7-Welding Fume-3.18 mg** | | | |
| 288.7 | C | 1420 | 14 |
| 534.0 | O | 4000 | 36 |
| 935.1 | Cu | 1350 | 4 |
| 1024.6 | Zn | 14240 | 75 |

## Table IX

## Data From Dust on Filters (Continued)

### Sample #1025-Black Filter

| Binding Energy(ev) | Element | Peak Intensity (c/sec) | Estimated wt.% |
|---|---|---|---|
| 287.0 | C | 2740 | 27 |
| 407.0 | N(nitrate) | 1400 | 17 |
| 532.2 | O | 8640 | 77 |

## IV. VALUE OF IEE TO HEALTH AND ENVIRONMENTAL STUDIES

The results given above on the submitted samples serve only as an indicator, and not final proof, of the type and quality of results that can be obtained from an IEE spectrometer. The strong feature of an IEE spectrometer is that it is sensitive to elements in a very thin surface layer, 50 to 100 Å in thickness. As a detector of ppm, or smaller, in a bulk sample, it is not competitive with other techniques, such as an emission spectroscopy. However, if the material of interest is normally on a surface, or can be prepared as a surface layer, then IEE will detect the elemental content and give quantitative and chemical character information of the elements present.

The value of IEE for the study of dust collected on filters is that no special chemical preparation or treatment of the sample is required. The results obtained are in terms of weight percent of an element in the dust collected on the filter. However, they do not give a measure of the total dust accumulated per volume of air passed through the filter. That result can be determined from a simple weight measurement. Since only a small total volume of dust is required, air sampling time can be minimized. The IEE spectrometer sees only a 50 to 100 Å thick layer, and there is no advantage in collecting more samples than that required to form a 100 Å thick layer. A sample volume of about $10^{-6}$ $cm^3$ is required to prepare an IEE sample to a depth of 100 Å.

Chemical contamination of surfaces is an area in which IEE could prove valuable. In principle, a wiping technique in which a suspected surface is wiped with a paper or cloth of known composition could be used. With the contamination trans-

[illegible] to the surface of the paper or cloth, a relatively [illegible] sample is available for examination by IEE. Again, no additional chemical treatment of the sample is required.

Because of the sensitivity of an IEE spectrometer to elements in a surface layer, contaminants in the ppm range can be determined in some problems involving solutions. A component of low vapor pressure which is present in a solvent of relatively high vapor pressure is required. As an example, we have observed 1 ppm of CaF in a standard prepared with [illegible] water. Polymers in water have also been observed in the parts per million range. In this technique, the solution is spread on a metal IEE sample plug and the volatile solvent is removed by gentle heating. A thin surface layer of the solvent of low vapor pressure remains. Quantitative results require that the volume of solution placed on the sample plug be measured. Sensitivity can be increased by applying more solution. A limitation of the procedure is that the sensitivity is reduced by surface [illegible] from components in the solution other than the desired component.

In the analysis of traces of contaminants in bulk materials, such as the cement samples examined, IEE spectrometry is now useful only to a range of about 0.1 weight percent.

The study of bulk lung tissue can be done adequately by IEE if the detection limits required are of the order of 0.1 weight percent of an element. In the detection range for which it is useful, no additional chemical treatment of the sample is required. Again, within its detection range, IEE has the advantage of detecting unsuspected elements. Rather than examine dried, pulverized lung tissue, more information might be obtained from an IEE examination of the excised surface of a lung which is exposed to air.

In all of the above applications decreased lower limits of detection are desirable. As will be discussed in Section V, we are awaiting delivery of an improved X-ray anode which will provide an improved signal-to-noise for the same scanning time.

## V. FUTURE IMPROVEMENTS IN INSTRUMENTATION AND METHODS

In addition to simply fulfilling this contract by running the samples supplied in a somewhat standardized procedure, we have considered the problem of how to optimize the data obtained along with minimum analysis time. The analytical problem can be defined as the determination, both quantitatively and qualitatively, with respect to identification and characterization of chemical environment, of all elements within the sample. Essentially all elements in the periodic table may be contained in your present or future samples.

The complete solution to the overall analytical problem defined above requires a large amount of information on all elements which is not available as yet. The qualitative identification of all elements in a wide scan requires a knowledge of the binding energies of all electron levels and Auger levels of all elements as observed by the particular spectrometer used. The binding energy table of Siegbahn is very useful, but, as discussed in the report, some of the values are not accurate enough for determinations in more complicated mixtures. A range of binding energies should be available for reference to correspond to binding energy shifts with oxidation states of an element. Ideally, one would like to have wide scans of all elements in all possible oxidation states. From such scans, all binding energy and Auger levels would be measured along with intensities of all levels. Such improved data are being collected as time permits.

A formidable problem is the effect of charge build up on insulated samples and the determination of true binding energies for such samples. For a set of similar samples, correction factors can be experimentally determined. Mixing of a conducting material with an insulating sample works well in some cases. Much work has been done at this laboratory and others to find the universal solution to this problem. At this point, no universally satisfactory solution is available. Correction factors are determined for a specific problem. One of the simplest procedures is to use the observed binding energy of the carbon line, which is almost always present as an impurity or surface contamination as methyl-methylene carbon, as an internal standard to correct binding energies.

Provisions for improvement of the sensitivity of the Varian induced electron emission spectrometer have been made during the past six months. Varian Associates are now manufacturing an improved magnesium X-ray anode capable of providing a much greater X-ray flux than our present aluminum anode. The X-ray flux from the new anode is increased through its ability to handle higher power and an improvement in the geometry of the anode which allows a larger fraction of the total flux produced to be focused on the sample. The result of these improvements is an increase in signal to noise of approximately 20 for identical scanning times. Conversely, the required scanning time for the present signal-to-noise level is reduced by a factor of 20. We ordered this new anode in October, 1971, with the understanding that we would be delivered in December of 1971. Delivery is now scheduled for the month of April.

An additional piece of equipment which allows one to handle wide scans of all elements more efficiently is the new 8K program for the IEE from Varian. One feature of this program is that a wide scan of 1000 volts can be called for with a single entry on the teletypewriter, and the entire 1000 volt region is automatically scanned sequentially in 100 volt segments. At the end of the scan, the entire scan can be plotted or any segment can be plotted. Any small region which contains a peak of interest can be expanded to any desired scale and plotted. This latter provision eliminates the need to rescan small sections of a wide scan to examine a particular peak. This feature would be of particular value for samples, such as yours, in which one cannot anticipate the elemental composition before scanning. Although our present 4K computer will not handle this program, I had an opportunity to run such a wide scan at the Varian exhibit at the Pittsburgh Conference in Cleveland.

## VI. CONCLUSION

The field of induced electron emission is a new but rapidly developing field of spectroscopy. The newness of the field is exemplified by the fact that during the life of this short contract, Varian has provided three improvements for our spectrometer: (1) a thinner X-ray shield for higher flux density, (2) a more linear counting preamp and pulse amplifier were installed and (3) wiring changes in the retarding voltage power supply were made to improve the accuracy of binding energy measurements. Unfortunately, with such rapid development, earlier data and techniques become rapidly outmoded. Much work remains to be done in the development of simple and general techniques for absolute binding energy measurements. Quantitative work needs improved understanding of what the spectrometer observes in the sample and related problems. However, with the broad interest shown by the rapidly increasing number of spectrometers in operation, development of techniques and applications should be rapid. The actual and potential applications to environmental problems have been discussed above, and merit your consideration.

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