Characterization of Arc Welding Fume

Research performed by the Mellon Institute Materials Characterization Center, Pittsburgh, Pennsylvania, under contract with the American Welding Society and supported by industry contributions.

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February, 1983

Prepared for:

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I. Introduction

During the process of welding, metal vapors are produced in the electric arc. As these vapors cool and solidify, a fume is formed that may be a potential health hazard to the welder and to others working in the same area. Such fine aerosols are all irritating to the respiratory system. Yet some fumes may potentially be more dangerous than others because of the specific substances present.

The purpose of this study is to provide a data base of chemical, crystallographic, and physical data for representative welding fume types which will aid in the understanding of the interactions of these particles with the human respiratory system. Such interactions are affected by many variables. Therefore, a simple percent weight analysis for various elements does not provide adequate information since individual particle size and chemistry affect toxicity. For example, a few large particles may dominate a percent by weight analysis. However, if these particles were over $10\,\mu M$ in diameter, they might not reach the lower respiratory system at all, while compounds present in thousands of fine particles would penetrate to the alveoli of the lungs and could be absorbed into the blood. Particle morphology is also significant since particles with sharp edges or fibers are more irritating to the lungs than smooth, sphere-shaped objects. Finally, specific compounds must be identified since such factors as crystallinity, solubility, and oxidation state affect toxicity. Such information may influence the determination of federal standards for occupational exposure.

These objectives were accomplished by using various macro and micro scale techniques. Initially, energy dispersive X-ray analysis (EDXA) and X-ray diffraction (XRD) were used to obtain background information on bulk fume properties. The focus of this work was the analysis of the welding fume on a particle by particle basis. Automated electron beam analysis (SPEC) was used to analyze large numbers of particles, and specially designed computer software sorted the particle data by size and chemistry. Finally, a scanning transmission electron microscope (STEM) was used for a manual examination of a smaller number particles for size, chemical composition, and crystallinity. An examination of all of the data available for a fume can then be used to decide whether toxicological testing may be advisable.

II. Sampling Techniques

Two general types of samples were required for the investigation: bulk fume samples which could be used for the analytical techniques requiring large amounts of sample material, and lightly dispersed samples for the techniques which provide analyses of individual particles.

A. Bulk Samples

The bulk samples were collected by AWS in a conical chamber as described in AWS F1.1-79, *Laboratory Method for Measuring Fume Generation Rates and Total Fume Emission of Welding and Allied Processes*. This provides a sample of several grams needed for certain analytical procedures such as X-ray diffraction.

B. Dispersed Samples

For the analytical techniques which provide data from individual particles of the fume, it is required that the particles be dispersed in such a manner that the individual particles are not contingent so that individual particle data is not altered by adjacent particles. In principle, this can be accomplished in two ways. One method would be to redeposit portions of bulk samples to provide a non-contingent dispersion. This approach, however, has some danger in that there is no absolute assurance that the redeposition process does not break up naturally occurring particle agglomerates, dissolve certain particle types, or lose either large or small particle sizes.

The other approach is to collect the particles in a dispersed state on a suitable substrate directly from the weld fume. The only concern about this approach is that the collection times are necessarily short (a few seconds) and may not accurately represent an 8-hour average.

Three direct sampling techniques were investigated in order to determine a method that would reliably sample representative portions of the various arc welding fumes.

1. Nuclepore Filter Samples

Fume samples were collected by suction (2 liter/min) onto polyester Nuclepore filters (pore size $0.2 \mu M$) loaded into standard plastic cassettes. There was some tendency for particles to agglomerate around the pores, but this was not a serious problem if sampling times were kept relatively short and the filter loadings were light. It was most convenient to collect several samples 18 inches above the arc at times such as 1, 3, and 5 seconds in order to bracket the optimum filter loadings needed for the various analytical techniques such as SPEC and STEM.

This technique is a standard method for collection of ambient air particulates analyzed in this laboratory. It also appears to be the best method for collecting fume samples defined for characterization of the individual particles rather than by bulk analysis.

2. Electrostatic Collector

With this technique, the particles were collected on smooth surfaces such as a glass slide or plastic tape using an electrostatic collector and charge neutralizer system. Although this technique reduced the tendency of the particles to agglomerate, the method was discarded because some agglomeration was still observed and because the long sampling tube needed for this instrument may be causing some size and chemical discrimination in particle collection. Further, it was felt that the electrostatic charge neutralizer in the system might be breaking up naturally-occurring agglomerates and, therefore, altering the actual state of the weld fumes.

3. Sticky Films

Samples were collected simply by holding a glass slide coated with a very thin film of a sticky substance such as Vaseline directly in the fume. This method was also discarded because the smallest particles are not representatively collected due to the air stagnation zone that develops at the surface of the slide.

Therefore, Method 1, the collection of the fume on Nuclepore filters, was selected as the primary sampling technique. The samples that were collected were compatible with the scanning electron microscope and the scanning transmission electron microscope, the instruments needed to measure size and chemistry of the submicron particles that are characteristic of welding fume.

III. Analytical Techniques and Sample Preparation

A. X-ray Diffraction (XRD)

Portions of the as-received bulk fume samples were loaded into glass trays to provide a smooth, even surface of the material. The trays were then placed in an X-ray diffractometer and exposed to copper K-alpha radiation over the Bragg reflection angle of 6 degrees to 100 degrees using a focusing graphite crystal, diffracted-beam monochromator. The output data from an X-ray diffraction analyses typically consists of peaks of different intensities at various Bragg reflection angles. These peaks result from the unique structures of crystalline materials with definite relationships of the distances and angles between the constituent atoms. Thus, proper indexing of the reflections from an X-ray diffraction pattern will reveal the specific crystalline compounds and phases which are present. It is important to mention that X-ray diffraction will not indicate the presence of amorphous materials or materials with particle sizes less than approximately 0.03 μM.

In the present study, the peaks on the patterns were generally relatively sharp indicating that at least portions of the sample materials were fairly well crystallized. The results of the analyses for the six samples are described in the Discussion Section of the report.

B. Energy Dispersive X-ray Spectrometry (EDXA)

Portions of the bulk samples were mounted on high purity graphite wafers with Duco Cement. coated with $0.02 \mu M$ of carbon. and examined in the scanning electron microscope (SEM) using a 24 KV accelerating voltage and a tilt angle of approximately 45 degrees. The microscope is equipped with an energy-dispersive X-ray analyzer which detects and semi-quantitatively measures all elements with atomic numbers greater than ten. (The elements not detected by EDXA are: hydrogen. helium, lithium, beryllium. boron. carbon, nitrogen. oxygen, fluorine, and neon. It is sometimes possible to detect fluorine if the concentration is at least 5 percent.) EDXA works by virtue of the fact that the high energy electron beam excites all elements in the sample and causes them to emit characteristic X-rays whose energies are unique to the emitting element. The X-rays are detected and energy-sorted by a solid-state detector, providing a spectral presentation of all elements present in concentrations greater than approximately one-half percent.

Further, the analysis can be confined to specific sample features as small as approximately 1 micron or, as in the present case, scanned over areas as large as approximately 4 mm x 4 mm to provide averages typical of the bulk concentration.

C. Suspended Particulate Evaluation and Classification (SPEC) System

The SPEC system combines three basic analytical instruments to produce its particle-by-particle particulate analysis. An electron beam image analyzer is joined to a scanning electron microscope (SEM) and an energy-dispersive X-ray analyzer (EDXA). The motion of the electron beam is digitized, allowing the position of the beam to be completely controlled by a mini computer. Using contrast variations resulting from differences in chemistries between the particles and the substrate, a description of particle size, shape, and chemistry can be rapidly generated and stored in a computer for the subsequent retrieval.

The fume samples were prepared for analysis by cutting a segment of approximately one square centimeter from the middle of the Nuclepore filter. These were mounted on an aluminum SEM stub using an amorphous graphite solution, then coated with approximately 0.02 μM of carbon by exposure to a carbon arc in vacuum. At least 1000 particles were analyzed for each fume type. Particle density on the filters ranged from 10^5 to 10^7 particles per square centimeter. Because of the random distribution of the fume particles, the analytical results are equivalent to those that would be obtained if all of the particles on the filter were analyzed.

The basic operational steps of the SPEC system are as follows:

- Generation of a search grid system
- Detection of particles intersecting the search grid system
- Size and shape analysis of particles
- Chemical analysis of particles
- Data reduction and particle type classification.

1. Generation of a Search Grid System

A digital scan generator is used to convert the normal SEM beam scanning motion of a stepping motion with regular intervals. The spacing between grid points is chosen in such a manner as to intersect a representative fraction of the particles on the SEM viewing screen. For this study, a grid size was selected such that all particles greater than $0.07 \mu M$ diameter would be detected 100 percent of the time. The grid size was chosen after examination of high magnification SEM and STEM pictures. Particles as small as $0.01 \mu M$ were observed, but the vast majority were $0.1 \mu M$ or larger. Subsequent analysis of particle size distribution graphs for the six fumes tested in this study indicated that particules smaller than 0.07 μM constituted 0.1 to 1 percent by weight and 1 to 25 percent by number. After the grid is defined, the computer instructs the electron beam to pause at each grid point while a particle detection is performed.

2. Detection of Particles Intersecting the Search Grid System

The particles are detected on the grid points by monitoring a backscattered electron signal. A signal above an adjustable threshold value indicates that the beam is on a particle. If the signal is below the threshold, the computer selects the next coordinate of the grid.

3. Size and Shape Analysis of Particles

After a particle is located, a subroutine is used to drive the beam in a preset pattern to determine the particle size and shape. The preset pattern consists of eight diagonals, each of which is terminated when a grid point is monitored and found to be off the particle. The pattern is repeated twice — once to locate the particle and once to determine the lengths of the diagonals through its centroid. The minimum diagonal becomes the particle Width. The maximum diagonal becomes the particle Length. Its Average Diameter is the arithmetic average of the eight diagonals. Finally, the data is stored and the beam is positioned to chemically analyze the particle.

4. Chemical Analysis of Particles

The chemical analysis of a particle is performed by a computer command which positions the electron beam at the measured centroid of the particle for a preset time, usually one or two seconds. The electron beam excites X-rays characteristic of all the elements present in the particle. All elements present in the particle above atomic number ten (neon) in the periodic table are detected simultaneously. Their signal levels are stored in the memory of the computer for subsequent retrieval. For this study, the following 18 elements were monitored: sodium, magnesium, aluminum, silicon, phosphorus, sulfur, chlorine, potassium, calcium, titanium, vanadium, chromium, manganese, iron, copper, zinc, bromine, and lead. Unfortunately, this original list of elements did not contain nickel, an element present in stainless steel. Therefore, the one stainless steel fume was reanalyzed using a 19-element file that monitored nickel.

5. Data Reduction and Particle Type Classification

Typically, a thousand particles per sample are analyzed. Additional information other than lineal dimensions is derived by calculating the volume and surface area. Each particle is assumed to be a prolate spheroid with the Length as the major axis and the Width as the minor axis.

The volume equation is:

$$V = \tfrac{4}{3}\pi ab^2$$

where: a = 1/2 Length
b = 1/2 Width

The surface area equation is:

$$S = 2\pi [b^2 + ab/e \, \mathrm{Sin}^{-1}e]$$

where: e, Eccentricity, $= [1 - (b^2/a^2)]^{1/2}$

Next, the particles are separated into different types based on present chemistries derived from the X-ray spectra.

Two new chemistry definition files have been developed for the present study — one for the ferrous base fumes containing thirty nine particle categories, the other for the aluminum base fume containing twenty one particle categories. These categories are expressed in elemental categories. These categories are expressed in elemental form, and not as compounds. EDXA identifies only elements with atomic number greater than ten. Therefore, low atomic number elements (e.g., oxygen, fluorine) are not mentioned in the chemical categories since they cannot be observed. It is to be understood, however, that the elements mentioned in a particular category are virtually always present as complex oxides and not as metals. In addition, fluorides may be present in certain fumes such as E7018 and E308-16, where fluorides were used as fluxes in the original welding consumable.

The ferrous base fume categories are:
(1) Carbon/Organic
(2) Iron
(3) Iron with Low Silicon
(4) Iron with High Silicon
(5) Iron-Manganese
(6) Iron-Chromium
(7) Iron-Chromium-Manganese
(8) Iron-Copper
(9) Iron-Vanadium
(10) Iron-Zinc
(11) Iron-Titanium
(12) Iron-Aluminum
(13) Iron-Sulfur
(14) Iron-Chlorine
(15) Potassium-Chromium
(16) Potassium-Iron
(17) Potassium-Chromium-Iron
(18) Calcium-Iron
(19) Potassium-Calcium-Iron
(20) Potassium-Manganese
(21) Potassium-Titanium
(22) Calcium-Chromium
(23) Calcium-Manganese
(24) Calcium-Titanium
(25) Potassium-Calcium
(26) Potassium-Rich
(27) Calcium-Rich
(28) Lead-Rich
(29) Chromium-Rich
(30) Manganese-Rich
(31) Copper-Rich
(32) Titanium-Rich
(33) Vanadium-Rich
(34) Iron-Rich
(35) Sodium-Rich
(36) Magnesium-Rich
(37) Aluminum-Rich
(38) Silicon-Rich
(39) Miscellaneous

The aluminum base fume categories are:
(1) Carbon/Organic
(2) Aluminum
(3) Aluminum-Copper
(4) Aluminum-Magnesium
(5) Aluminum-Iron
(6) Aluminum-Silicon
(7) Aluminum-Chromium
(8) Aluminum-Titanium
(9) Aluminum-Vanadium
(10) Aluminum-Sulfur

(11) Aluminum-Chlorine
(12) Aluminum-Potassium
(13) Aluminum-Calcium
(14) Aluminum-Manganese
(15) Copper-Rich
(16) Chromium-Rich
(17) Manganese-Rich
(18) Iron-Rich
(19) Magnesium-Rich
(20) Aluminum-Rich
(21) Miscellaneous

Category definitions can range from very specific to very general. For example, a particle identified as *Iron* shows an iron peak with a relative X-ray intensity of at least 85 percent. It is to be understood that the iron is present as an oxide. Other elements are present only in trace amounts. For the "Iron with Low Silicon" category, up to 50 percent may come from silicon with the rest from iron. Other elements are present only in trace amounts. For "Iron with High Silicon", silicon produces 50 percent or more of the X-rays. Again, these are complex mixtures of iron oxides and silicon oxides. For categories such as "Iron-Manganese" or "Iron-Titanium", the elements mentioned may be present in any proportion. These categories also allow for aluminum and silicon to be present. Specific definitions were developed when an analysis of the particle-by-particle printout showed that these species were present in relatively large numbers. Other particles are collected into more generally defined categories such as "Chromium-Rich" or "Copper-Rich". The element mentioned will produce at least 25 percent of the X-rays, but particules such as Copper-Phosphorus, Copper-Manganese, and Copper-Silicon will all be collected into the same Copper-Rich category.

The Carbon/Organic category collects particles composed of elements of atomic numbers less than ten, primary carbonaceous material, and the final Miscellaneous category collects those which do not fit into any previous category. After the particles are sorted by chemical category, the program completes its work by calculating size distributions for each particle type and for the whole sample.

The specific definitions of the categories will be found in Tables 1 and 2.

In addition, the data was re-analyzed to investigate the distribution of specific elements: copper, chromium, lead, and manganese. Only three simple categories were used: High, with the element producing over 50 percent of the X-rays; Medium, 25-50 percent; and Low, 1-24 percent. The Miscellaneous category then collected all of the particles that did not contain that element.

D. Transmission Electron Microscopy (TEM) and Scanning Transmission Electron Microscopy (STEM)

Samples for the TEM and STEM were prepared by overlaying a portion of the Nuclepore collection filter with approximately $0.02 \mu M$ of carbon by evaporation. The fume particles were retained in the carbon film while the filter substrate was dissolved in chloroform. The carbon film was transferred to a standard 300 mesh copper TEM grid. The grids were washed in chloroform before use. The grid and sample were washed again to insure complete removal of the filter media. The STEM was used to obtain electron diffraction and EDXA date.

The prepared grids of each fume were examined in a scanning transmission electron microscope operating at 120 kV. The microscope was equipped with an energy dispersive X-ray analyzer.

STEM analysis was undertaken because it can obtain morphological, chemical and crystallographic information from the same region. While it thus has a great potential for this type of problem, it is inherently more time-consuming than the SPEC analysis, and it was realized that it could not be compared statistically with the SPEC data. The approach chosen, therefore, was to perform analyses on 5-10 particles per fume to determine if the chemistries detected by SPEC could be directly related to the crystal structures determined by XRD. The identification of electron diffraction patterns is, in many cases, more ambiguous than X-ray patterns since only a single slice of reciprocal space is obtained in a single pattern. For this reason, the crystal structures were not determined directly from the electron diffraction data. Instead, the electron diffraction patterns were indexed against the structures observed by XRD.

Of the several modes of electron diffraction available in the STEM, convergent beam diffraction in the TEM mode was chosen. In this technique, the electron beam is focused down to a spot about $0.1 \mu M$ in diameter which is then placed on the particle to be analyzed. In this way, the electron diffraction pattern and the X-ray spectrum of the particle were recorded simultaneously. The X-ray spectrum records the elements present. The diffraction pattern determines the crystal structure and interatomic distances. Particular compounds are identified by indexing this data against values for known substances. While smaller spot sizes are attainable in this type of instrument, they were not used here for two reasons. First, they produce a high contamination rate on the specimen which leads to a rapid deterioration of the diffraction pattern and second, the angle of view in the diffraction pattern is somewhat restricted.

The particles analyzed in each fume were about $0.1 \mu M$

in diameter or larger. The particles were chosen to encompass the range of morphologies observed. Since the diffraction data was important, many particles of each type were often examined before one with a diffraction pattern suitable for indexing was found. Then the X-ray spectrum was taken and the particle's image recorded. In some cases no satisfactory diffraction patterns could be obtained for any of the particles in a given morphological class. This occurred both for particles that were too small (so that diffraction patterns showed spots from too many individual particles) and too thick (so that the transmitted intensity was too weak or non-existent).

Because of the relatively complex structure of some of the phases, the indexing of the electron diffraction patterns was performed with the aid of a computer program.

E. Gas Chromatography-Mass Spectrometry (GC-MS)

During the analysis of size and chemistry by the SPEC system, a portion of the particles could not be classified by chemical composition because they yielded an X-ray count below the threshold limit. This could result from a very small particle that did not produce enough X-rays to trigger the detector or from a particle containing carbon compounds that would not be detected by EDXA.

Since carbon combustion products can be carcinogenic, a brief study was undertaken to eliminate the possibility of these substances existing in the fume. 0.5-gram samples of two of the bulk fumes (E7018 and E70S-3) were extracted with 20 ml of dichloromethane for 8 hours using a Soxhlet extractor. The solvent was concentrated to one milliliter, and a portion of this concentrate was analyzed by GC-MS. No organic compounds were observed. Thus, it is more likely that the unclassified particles are simply too small for a good EDXA analysis. [AWS comment: Organics would not be expected to be present because of composition when exposed to arc temperatures that can exceed 6000°K.]

IV. Results and Discussion

The fumes from six different types of welding rods and wires have been analyzed to determine the size and shape of the particles and the crystalline phases present. These included low carbon steel solid, coated, and flux cored rods and wires (E6010, E7018, E70S-3, E70T-1), a stainless steel coated rod (E308-16), and an aluminum wire (E5356). The properties of the bulk fumes were analyzed by EDXA and X-ray diffraction. Then, particles collected on Nuclepore filters were analyzed for their in-

dividual size and chemistry. Data for approximately 1000 particles were stored on floppy disc and size distributions by number, by surface area, and by mass were calculated. Finally, selected particles were examined by electron diffraction using STEM analysis.

In the following sections, the data from the SPEC system are compared with other properties, such as the EDXA spectra and crystalline compound/phase constituents. SEM photographs of the fumes are shown in Figs. 1a through 1f, EDXA spectra in Figs. 2a through 2f. Table 3 lists the size distributions for the total fume sample from the SPEC analysis by number, by surface area, and by mass. Table 4 shows the average particle diameters for the total fume sample. Values for percent composition by category are given in Tables 5a through 5e for the steel fumes. Tables 6a through 6e list size distributions by number, and Tables 7a through 7e list size distributions by mass for the steel fumes. Average values for diameter, volume, and surface area by category are given in Tables 8a through 8e for the steel fumes. Data for the aluminum fume given in Tables 9a through 9d. The composition of these fumes by standard wet chemical analysis techniques is given in Table 10.

A. Particle Size

The particle size distributions were similar for all six fumes and can be discussed together. (Graphs of the size distributions by number, by surface area, and by mass are given in Figs. 3-8.)

The particles were all very small. Less than 1 percent of the particles were larger than $1\mu M$ (see Figs. 9-14). The largest particle observed was $2.8\mu M$. STEM pictures showed that particles as small as $0.01\mu M$ exist. A study done by the Task Group on Lung Dynamics in 1966 indicated that particles approximately 5 to 10 μM or smaller are respirable. The exact point varies with the individual. Thus, all of the fume particles observed were in the respirable range.

The size distributions for the six fumes tested were all very similar. There seems to be little variation with the type of welding consumable or with individual particle chemistry.

For example: Number Average Diameter 0.14-0.33 μM
Area Average Diameter 0.21-0.41
Volume Average Diameter 0.34-0.64

There is little variation in average diameter among the chemical categories within a given fume.

For example: E6010 0.09-0.54 μM
E70S-3 0.06-0.30
E308-16 0.06-0.27

The reverse is also true. There is little variation among the different fumes for a given chemical category.

For example: Fe $0.14-0.17\,\mu M$
                Fe-Mn $0.13-0.20$
                K-Fe $0.11-0.18$

None of these size variations would greatly influence the amount of each type of material that reaches the lower respiratory system.

The particles from all six fume types seem to obey the log normal distribution. This can be seen from the straight lines produced when the values for cumulative percent composition (for particles less than $1\,\mu M$) are plotted against the log of the particle diameter on probability graph paper. (See Figs. 3 through 8 and Tables 3 and 4.) Values for the geometric mean diameters are located at the points where the lines intersect 50 percent. For these graphs, $1\,\mu M$ was used as an arbitrary upper limit. Ninety nine percent of the particles are less than $1\,\mu M$ in diameter. There are so few particles greater than $1\,\mu M$ that average diameters derived from this data would not be statistically significant.

B. Particle Chemistry

The chemical composition of the fumes was evaluated by three methods: X-ray diffraction of the bulk fume, STEM analysis of a few individual particles, and SPEC analysis of a large number of particles. A wet chemical analysis was also provided by the AWS. These particles appeared as spheres or as chains or clusters of spheres. Some appeared to be just touching, attracted by static electricity or by magnetic forces. Others appeared to have fused at high temperatures. Even though no crystal planes were evident, particles examined by STEM produced electron diffraction patterns, indicating that crystalline material was present. Some of the particles might even be single crystals.

1. E6010

The wet chemical analysis showed 46.0 percent iron, 4.0 percent manganese, 6.3 percent sodium, 7.5 percent silicon, and 0.2 percent titanium. Analysis of the elements present in the bulk sample by EDXA showed a large amount of iron, intermediate amounts of silicon and manganese, and a trace amount of titanium. XRD of the bulk sample showed that the major crystalline phase was magnetite (Fe_3O_4).

The SPEC system was used to analyze approximately 1000 individual particles by chemistry and by size. The mean diameter (by number) for all particles was $0.192 \pm 0.146\,\mu M$. The main categories identified by the computer search are shown in the following table.

			E6010 Composition by Category		
Category	Percent by Number	Average Diameter	Composition (Volume Weighted X-ray %)		
3. Fe/Low Si	31%	$0.188\,\mu M$	Si(36)	Mn(4)	Fe(56)
4. Fe/High Si	10	0.245	Al(21) Si(46)	K(9)	Fe(21)
5. Fe-Mn	16	0.202	Si(36)	Mn(14)	Fe(44)
18. Ca-Fe	8	0.169	Si(37)	Ca(13)	Fe(43)

Chromium is present at low concentrations in 7 percent of the particles. The chromium seems to replace iron in the various types of iron-silicon particles. Copper is present at low concentrations in 3 percent of the particles and it is also found in iron-silicon mixtures. Lead is present at low concentrations in only 2 percent of the particles containing aluminum, silicon, potassium, and iron. The behavior of manganese is similar to chromium and copper. Thirty percent of the particles contain some manganese in mixtures of iron and silicon. Only 0.5 percent of the particles contain intermediate amounts of manganese. These are also iron-silicon-manganese mixtures, and pure manganese oxides is unlikely to exist. (Details of the other particle categories are given in Tables 5a, 6a, 7a, and 8a.)

STEM analysis showed particles that were predominantly iron with varying amounts of manganese and silicon. All of the electron diffraction patterns were indexable as $(Fe,Mn)_3O_4$.

Only 3 percent of the particles were categorized as "Iron," probably as Fe_3O_4. Nearly half of the particles were iron-manganese oxides listed either as "Fe/Low Si" or "Fe-Mn". A pure manganese oxide is unlikely to exist since no particles with a very high manganese concentration were observed. Even though most particles contained some silicon, no crystalline silica or transition metal silicates could be detected. Particles analyzed by STEM contained iron with varying smaller amounts of manganese and silicon. (See Fig. 9.) However, all of the electron diffraction patterns are similar, indicating a mixed iron-manganese oxide $(Fe,Mn)_3O_4$. Silicon must be present either as an amorphous oxide or in solid solution in the magnetite lattice. The water glass binder of the electrode contains sodium and perhaps potassium oxides and silicon dioxide. Other silicates and ferro-silicon are also present. These and all other materials in the electrode are partially vaporized by the arc and interact to form new compounds as the fume condenses. Iron compounds appear to crystallize, but the silicon compounds do not. Thus, a particle in the "Fe/High Si" category is probably a magnetite sphere either coated with condensed amorphous silicate or fused to another sphere which is primarily amorphous silicate. Particles in the "Ca-Fe" category are mixtures of magnetite and binder containing a calcium im-

purity. Although sodium is known to be present in the binder. it does not appear in any SPEC chemical category. Elements are detected by EDXA in the SPEC system. Sodium can be detected. but the sensitivity is low. When X-rays from very small particles are counted for short times (1 second). the likelihood for observing Na above background noise is not very good.

2. E7018

The wet chemical analysis showed 0.9 percent aluminum. 20.6 percent calcium. 19.5 percent fluorine. 24.6 percent iron. 12.5 percent potassium. 4.6 percent manganese. 3.3 percent sodium. and 2.8 percent silicon. Analysis of the elements present in the bulk sample by EDXA showed major amounts of potassium. calcium and iron, intermediate amounts of silicon and manganese, and trace amounts of aluminum. sulfur. and chlorine. XRD analysis of the bulk sample showed that the major crystalline phase is potassium-calcium fluoride. KF-CaF_2. Intermediate phases include magnetite. Fe_3O_4. calcium fluoride. CaF_2. and jacobsite. $MnFe_2O_4$. It should be mentioned again that the element fluorine. although prominent in the crystal phases, is very difficult to detect by EDXA.

The SPEC system was used to analyze approximately 1000 particles by chemistry and by size. The average diameter (by number) for all particles was 0.182 ± 0.117 μM. The categories identified by computer search are shown below.

E7018 Composition by Category

Category	Percent by Number	Average Diameter	(Volume Weighted X-ray %)
16. K-Fe	14%	0.179 μM	Si(18) K(36) Fe(28)
18. Ca-Fe	15	0.158	Al(7) Si(17) Ca(25) Fe(37)
19. K-Ca-Fe	48	0.188	Al(4) Si(10) K(28) Ca(22) Fe(23)

Chromium. copper. and manganese are present in the particles in low concentrations in 8. 8. and 23 percent. respectively. These elements are found in mixtures of the particles classified in the three main categories. In a typical particle, for example. X-ray percentage may be either 35 Ca, 14 Cr, and 51 Fe, or 22 Si, 15 K, 14 Ca, 21 Mn, and 27 Fe. Lead is found in low concentrations in only 5 percent of the particles in mixtures similar to those described above. (Details of the other particle categories are given in Tables 5b, 6b. 7b. and 8b.)

The STEM analysis of this fume was made difficult by the irregularities of the particles. They were either too thick to obtain diffraction patterns or. where thin enough. appeared to be multi-crystalline giving diffraction patterns too irregular to be indexable. Occasionally. particles could be found that showed only an Fe peak (see Fig. 10). These

patterns were again consistent with Fe_3O_4.

The particles in this fume are mixtures of potassium/calcium fluorides and iron/manganese oxides. Fe_3O_4 and $MnFe_2O_4$ are observed and probably non-stoichiometric oxides of iron and manganese are present as well. No pure manganese oxide is likely since particles with a very high Mn concentration are not found. No crystalline silicon compounds are observed. and the behavior of silicon is similar to that discussed for the E6010 fume.

3. E70S-3

The wet chemical analysis showed 0.4 percent copper. 57.0 percent iron, 7.8 percent manganese, and 3.3 percent silicon. Analysis of the elements present in the bulk fume by EDXA showed the elements iron and minor amounts of silicon and manganese. XRD analysis of the bulk sample showed that the major crystalline phase was magnetite. Fe_3O_4. XRD also indicated a trace of metallic iron.

The SPEC system was used to analyze approximately 1000 particles by chemistry and by size. The average diameter (by number) for all particles was 0.135 ± 0.114 μM. The main categories identified by the computer search are shown below.

E70S-3 Composition by Category

Category	Percent by Number	Average Diameter	Composition (Volume Weighted X-ray %)
2. Fe	9%	0.153 μM	Si(7) Fe(90)
3. Fe/Low Si	14	0.173	Si(10) Mn(6) Fe(76)
5. Fe-Mn	17	0.129	Si(12) S(4) Mn(13) Fe(62)
6. Fe-Cr	5	0.129	Si(16) Cr(10) Fe(53) Zn(5)
12. Fe-Al	6	0.103	Al(18) Fe(69)
16. K-Fe	6	0.111	Si(6) K(16) Mn(6) Fe(58)
18. Ca-Fe	10	0.118	Al(7) Si(13) Ca(15) Mn(5) Fe(48)
34. Fe-Rich	8	0.148	Al(4) Si(5) K(6) Fe(71)

Copper. chromium. and lead are found in low concentrations in 8, 10, and 7 percent of the particles, respectively. Once again, these trace elements are not found as a small number of particles of the pure oxide, but rather spread in small amounts through a large number of particles. For example, in the bulk fume 0.4 percent by weight is copper (see Table 8). Yet copper is found in 8.5 percent of the particles which make up 13.3 percent by weight of the fume sample analyzed by SPEC. Manganese comprises 7.8 percent by weight of the bulk fume. but 25 percent of the particles contain manganese at low concentrations in mixtures of iron. manganese. and silicon. An additional 3 percent contain intermediate amounts of manganese in particles of similar chemistry. It is unlikely that pure oxides of manganese are present. (Details of the other particle types are given in Tables 5c, 6c. 7c. and 8c.)

STEM analysis showed particles containing iron with 6-12 percent manganese and 3-7 percent silicon. The crystal structure of all of the particles was the same (space group FD3M) and could be indexed as $(Fe, Mn)_3O_4$. (See Fig. 11.)

This fume is quite similar to the E6010. Most of the iron exists as Fe_3O_4. Other transition metals easily substitute for iron in the magnetite lattice. Manganese is most commonly observed in these substitutions since its concentrations are the highest. Manganese constitutes 8 percent by weight of this fume, but no individual particles with a very high Mn concentration were found, indicating that a pure Mn oxide is unlikely. Other transition metals, present at even lower concentrations, are also not likely to be found as the pure oxide. For example, copper was found in low concentrations in 8 percent of the particles even though it made up only 0.4 percent by weight of the fume. Copper then exists as a very dilute (Fe, Cu) Fe_2O_4 solid solution. The XRD data also showed a weak peak that resulted from the presence of traces of metallic iron. This is the only fume in which the metallic form of an element was observed.

In the original electrode, silicon was present in the steel, not as an amorphous water glass binder. Nevertheless, no crystalline silica or silicates were observed. Silicon appears to become trapped in the rapidly condensing magnetite fume, possibly substituting for iron at random sites. It is also possible that amorphous silicates are present which cannot be detected by the methods used in this study.

4. E70T-1

The wet chemical and analysis showed 38.1 percent iron, 0.3 percent potassium, <u>11.1 percent manganese</u>, 8.9 percent sodium, 5.1 percent silicon, and 0.8 percent titanium. Analysis of the elements present in the bulk fume by EDXA showed iron and manganese, an intermediate amount of silicon, and trace amounts of sodium and titanium. XRD analysis of the bulk fume showed that the major crystalline phase was jacobsite, $MnFe_2O_4$ with an intermediate amount of magnetite, Fe_3O_4.

The SPEC system was used to analyze approximately 1000 particles by chemistry and by size. The average diameter (by number) was $0.163 \pm 0.126 \mu M$. The main categories identified by the computer search are shown below.

E70T-1 Composition by Category

Category	Percent by Number	Average Diameter	Composition (Volume Weighted X-ray %)			
2. Fe	14%	$0.140 \mu M$	Fe(99)			
3. Fe/Low Si	25	0.160	Si(25)	Fe(72)		
5. Fe-Mn	37	0.178	Si(8)	Ti(11)	Mn(19)	Fe(59)

Manganese is present in just over half of the particles. Thirty two percent contain low amounts of manganese and are similar to the "Fe-Mn" particles described above. 18 percent contain intermediate amounts of silicon, iron, and manganese. One percent of the particles contain over 50 percent manganese. Half of these particles are mixtures of iron and manganese, or iron, manganese, and silicon. The others seem to be a mixture of manganese and silicon. These may be a manganese silicate or a manganese oxide covered with an amorphous silica layer. However, the small number of these particles makes their exact identification impossible by techniques such as XRD or STEM.

Copper, chromium, and lead are present in low concentrations in 1, 2, and 0.5 percent of the particles, respectively. Particles with higher concentrations of these elements are present in less than 0.5 percent of the particles. They are, in general, included in mixtures of iron, manganese, and silicon. (Details of other particle types are given in Tables 5d, 6d, 7d, and 8d.)

STEM analysis showed particles containing iron with 6-12 percent manganese. Only two particles contained silicon (3-4 percent). The crystal structure of all of the particles was the same (space group FD3M) and could be indexed as $(Fe, Mn)_3O_4$. (See Fig. 12.)

In fumes in which the manganese to iron ratio is low, no particles with a high manganese concentration are observed. On the other hand, if the manganese to iron ratio is high enough, manganese oxides may form. In the E70T-1 fume the Mn/Fe ratio is 1/3.5 by wet chemical analysis. One percent of the particles contained manganese in large amounts (>50 X-ray percent). Since the other oxides present $(Fe_3O_4, MnFe_2O_4)$ have the X_3O_4 stoichiometry, Mn_3O_4 may be present, but in concentrations too small to be observed by XRD. No crystalline silicates were observed. Silicon is present either as an amorphous silicate or in solid solution in the metal oxides.

5. E308-16

The wet chemical analysis showed <u>5.6 percent chromium</u>, 16.8 percent fluorine, 10.8 percent iron, 18.9 percent potassium, <u>6.2 percent manganese</u>, 10.4 percent sodium, 0.75 percent nickel, and 4.9 percent silicon. Analysis of the elements present in the bulk fume by EDXA showed silicon, potassium, chromium, manganese, and iron with trace of fluorine, sodium, and titanium. XRD analysis of the bulk fume showed mixed oxides of manganese and iron $(Fe, Mn)_3O_4$ and $MnFe_2O_4$, jacobsite. Transition metals were also observed as potassium salts, potassium chromate, K_2CrO_4, and potassium ferrate, K_2FeO_4. Villiaumite, NaF, was present in intermediate amounts.

The SPEC system was used to analyze approximately

1000 particles by chemistry and by size. The average diameter (by number) was $0.160 \pm 0.090 \mu M$. The main categories identified by computer search are shown below.

		E308-16 Composition by Category	
Category	Percent by Number	Average Diameter	Composition (Volume Weighted X-ray %)
5. Fe-Mn	5%	0.166μM	Si(32) Ti(5) Mn(26) Fe(26)
15. K-Cr	5	0.155	Al(6) Si(19) K(31) Cr(17) Mn(9)
16. K-Fe	18	0.169	Si(22) K(27) Mn(10) Fe(22)
17. K-Cr-Fe	5	0.176	Si(14) K(28) Ti(10) Cr(24) Fe(21)
18. Ca-Fe	7	0.144	Si(24) Ca(18) Mn(12) Fe(23)
19. K-Ca-Fe	7	0.159	Si(25) K(20) Ca(15) Mn(6) Fe(17)
20. K-Mn	8	0.161	Al(6) Si(25) K(29) Mn(22)
26. K-Rich	7	0.174	Si(26) Cl(5) K(50) Ca(5)
38. Si-Rich	6	0.161	Si(56) S(8) K(8)

Copper is present in low concentrations (12 X-ray percent) in 7 percent of the particles and in medium concentrations (28 X-ray percent) in 1 percent of the particles. These are primarily K-Cu or K-Fe-Mn-Cu particles. Lead is present in low concentrations in 6 percent of the particles. These are composed of K, Fe, Mn, and Pb. Only 1 percent contained mixtures of chromium and lead (together with iron and manganese) that might be present as lead chromate. Chromium is present in low concentrations in 16 percent of the particles and in medium concentrations in 5 percent of the particles. These appear to be K_2CrO_4 or mixtures of K_2CrO_4 and K_2FeO_4. In addition, slightly less than 1 percent of the particles contained nearly pure chromium oxide. Manganese was present in 40 percent of the particles. Thirty percent contain low amounts of manganese usually in particles which would be categorized as "K-Fe" or "K-Cr." Nine percent contained intermediate amounts of manganese, usually as "K-Mn" and "Fe-Mn" particles. One percent of the particles contained high concentrations of manganese. Some of these particles are mixtures of metal oxides (Mn with Fe, V, Cu). However, in this fume, particles of pure manganese oxide are observed in very small numbers (0.4 percent). Once again the very small numbers of these particles make their location and identification very difficult. (Details of the other particle categories are given in Tables 3e, 4e, 5e, and 6e.)

Since nickel was not among the elements in the original analysis, the stainless steel fume was reanalyzed to look for nickel-bearing particles. Nickel was observed in low concentrations in 2 percent of the particles. Like copper at low concentrations, nickel seems to be substituting for the more abundant transition metals in Fe_3O_4 or $K_2(CrFe)O_4$.

The STEM data for this fume differed from those discussed previously because of the elemental complexity of the particles analyzed. For example, Fig. 13 shows a particle high in Cr, Ca, and S with smaller amounts of

Fe, Mn, K, and Na. In no case was nickel detected. No identifiable diffraction patterns could be obtained for any of these particles.

The E308-16 fume was the most complex examined. Fluroine was observed (XRD) only as NaF, although it is not impossible that other alkali fluorides are present. The "K-Rich" category is probably KF. Iron and manganese are again observed as $(Fe,Mn)_3O_4$. The Mn/Fe ratio is only one-half by wet chemical analysis. One percent of the particles contained high manganese concentrations and Mn_3O_4 may be present. The nickel in the stainless steel fume, like copper in the E70S-3 fume, is present only in low concentrations, probably as $(Fe,Ni)Fe_2O_4$. Chromium exists as a $K_2(Fe,Cr)O_4$ solid solution. Manganese is probably also present in this solution. Some $KMnO_4$ may also exist since a few percent of the particles are categorized as "K-Mn", although other explanations are possible. The Cr/Fe ratio is also one-half. One percent of the particles contained Cr in high concentrations (>50 X-ray percent). These may well be a chromium oxide, although the concentration was too small to be observed by XRD. Another one percent of the particles contained mixtures of Pb and Cr and may be $PbCrO_4$. Once again no crystalline silicates are observed.

6. E5356

The wet chemical analysis showed 45.0 percent aluminum, 0.5 percent copper, 0.2 percent iron, and 5.4 percent magnesium. EDXA analysis of the elements present in the bulk sample showed a large amount of aluminum with trace amounts of iron and copper. The XRD data from the bulk sample showed that the major crystalline phase was α-alumina (Al_2O_3). Smaller amounts of magnetite (Fe_3O_4) and $(Cu,Fe)Al_2O_4$ were present.

The SPEC system was used to analyze approximately 1000 individual particles by chemistry and by size. The average diameter (by number) for all particles is $0.328 \pm 0.201 \mu M$. The main categories identified by the computer search are shown below.

		E5356 Composition by Category	
Category	Percent by Number	Average Diameter	Composition (Volume Weighted X-ray %)
2. Al	86	0.327 μM	Al(99)
3. Al-Cu	7	0.318	Al(65) Cu(35)

Chromium, manganese, and lead are not present in this fume. Copper is present in 8 percent of the particles although it is present only 0.5 percent by weight (Table 10). However, the distribution of copper contrasts con-

siderably with that observed in the steel fumes. In the steel fumes. copper is present at low concentrations. presumably substituting for iron in the crystal lattice. In the E5356 fume. only 1 percent of the particles had a low Cu concentration (20 X-ray percent). Five percent had a medium copper concentration (32 X-ray percent) and 2 percent had a high Cu concentration (64 X-ray percent). At least half of these particles contained nearly pure copper. probably as the oxide.

STEM analysis of this fume showed all of the particles to be Al_2O_3 without any detectable Mg. A typical spectrum is shown in Fig. 14 which has been expanded along the horizontal axis so that the shape of the aluminum K-alpha peak can be clearly seen. The K-alpha marker for magnesium is also shown in this Figure to indicate where magnesium would appear if present.

Only one aluminum fume was examined. Most of the fume (80 percent by weight) was a-alumina. Copper was present as an aluminate $(Cu,Fe)Al_2O_4$. Two percent of the particles contained Cu in high concentrations and may contain a copper oxide although this could not be detected by XRD. The magnesium present in this fume is not well characterized. No Mg compounds were observed by XRD or STEM. Few particles containing magnesium were identified by the SPEC system. In EDXA, the signal from magnesium at 1.25 KeV lies next to that from aluminum at 1.49 KeV. The strong peak from aluminum may be masking the magnesium signal. A second explanation is also possible. The sensitivity of EDXA for sodium and magnesium is low. (See the discussion of sodium in Section 1.) The small particle size and short counting times make the observation of these elements difficult. However, using new software developed since these fumes were analyzed, it may be possible to improve the ability to detect these two elements. Most of the Mg containing particles found in the SPEC analysis were Mg/Al combinations and may be a mixed oxide such as $MgAl_2O_4$.

V. SUMMARY

The welding fumes were composed of very fine particles with a log normal size distribution and average diameters in the easily respirable range of 0.1 to 1.0 μM.

Average particle size does not vary greatly among the fumes examined.

The particles appeared as individual spheres or as clusters of spheres that have been fused at high temperatures. The planes and angles that characterize crystalline material that has cooled slowly were absent in these particles. Nevertheless, much crystalline material was present. Every particle examined by STEM produced an electron diffraction pattern. Some patterns indicated that the particle was a single crystal. Others showed the complex overlapping patterns characteristic of the presence of several crystals within a single particle.

For the ferrous fumes. particle chemistry was dependent on the iron content of the fume. When large amounts of iron are present. the main crystalline phase is magnetite and other transition metals exist as $(Fe,X)_3O_4$. Only when the iron concentration is relatively low, is there a possibility that pure oxides of other transition metals are present. Other oxidation states for iron may then be present also, such as the $K(Fe,CR)O_4$ found in the stainless steel fume.

If fluorides were present in the original consumable, then sodium. potassium, and calcium fluorides were found in the fume. No transition metal fluorides were detected.

Crystalline silica and transition metal silicates were also not observed in the fume. The silicon either formed an amorphous silica or was in solid solution with the iron oxide.

Only one non-ferrous electrode was treated. an aluminum wire. The major fraction of this fume was alumina. Al_2O_3. Other elements present in small concentrations in the starting material reacted to form aluminates, XAl_2O_4.

This study has shown that automated electron beam image and chemistry analysis (SPEC) used with bulk X-ray diffraction and micro electron diffraction (STEM) techniques is an effective method for screening welding fumes for potential health hazards. The composition of the fumes from several different ferrous electrodes was similar. Therefore, a single list of chemical categories for the SPEC system can be tailored to identify particle types in a wide variety of fumes. A detailed analysis of all of the data can then be used to describe the behavior of all of the elements in the fume, even those present at low concentrations.