ENVIRONMENTAL CONDITIONS IN

U. S. COPPER SMELTERS

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An overview is presented of environmental conditions in the copper smelters operating in the United States through 1973 with data collected from surveys of the eight primary smelters. Airborne concentrations are included for arsenic, lead, zinc, copper, cadmium, molybdenum, and sulfur dioxide. Concentrations determined in the urine of smelters are included for arsenic, lead, copper, and cadmium. Airborne concentrations of sulfur dioxide were relatively high and variable in all smelters whereas concentrations of lead, zinc, cadmium, and molybdenum were consistantly low. Airborne copper concentrations were relatively high in certain areas but occured mostly as a non-respirable dust. Urine concentrations were not significantly higher than normal for arsenic, lead, and cadmium. The pararosaniline method and the hydrogen peroxide method are described for determining sulfur dioxide in the atmosphere.

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ABSTRACT

This report is an overview of environmental conditions in the copper smelters operating in the United States through 1973. The data, combined into industry-wide averages, was collected from six extensive and detailed surveys and eight surveys of a more superficial nature.

Airborne concentrations are included for arsenic, lead, zinc, copper, cadmium, molybdenum, and SO_2. Concentrations determined in the urine of smelterers are included for arsenic, lead, zinc, copper and cadmium. The data is presented in a manner intended to be indicative of concentrations which might be found over a several-year period throughout the industry, not necessarily relecting the concentrations which might be determined in a specific smelter at a given time.

Airborne concentrations of SO_2 were determined to be relatively high and quite variable in all smelters, whereas the concentrations of lead, zinc, cadmium and molybdenum were consistently low. Airborne copper concentrations were found to be relatively high in certain areas but it was concluded that most of the copper occurred as a "non-respirable" dust. The potential for arsenic-induced cancers may exist in the industry even though the atmospheric concentrations contraindicate a problem in regard to the usual acute effects.

Urine concentrations did not indicate significantly higher than normal exposures for those elements where urine analysis is meaningful, i.e., arsenic, lead, and cadmium.

INTRODUCTION

There are fifteen primary copper smelters in the United States (Table 1) which together employ about 5,000 workers who are directly engaged in the smelting process. These facilities process copper ores to recover copper and trace elements such as molybdenum, selenium, gold, and arsenic. All but two are located in five western states and most of them were originally constructed over 50 years ago. The basic processes employed have changed little in decades. The workers are potentially exposed to a variety of toxic and irritating gases and dust and, therefore, the question of occupational health problems in the industry has been the subject of several published reports, e.g., Pinto and McGill,[1] Pinto and Bennett[2] and Lee and Fraumeni.[3] These reports were of investigations of the causes of death in smelter workers and, while they pointed to the existence of environmental problems in the specific facilities concerned, could not be considered to be descriptive of conditions in the industry as a whole. In PHS Publication 1531, "Occupational Characteristics of Disabled Workers by Disabling Condition," smelterers are included in the group of furnacemen, smelterers, and pourers. For this group, the proportionate morbidity ratio from emphysema was 1.36, which is interesting but not interpretable because several occupations are included in this category. No studies of the morbidity experience of smelter workers per se have been reported.

In 1965 and again in 1969 at the request of the State of Montana, the United States Public Health Service's Western Area Occupational Health Laboratory, located at Salt Lake City, Utah, conducted environmental surveys of the Anaconda Company's copper smelter, at Anaconda, Montana. Also in 1969 a similar survey was done at Kennecott Copper Corporation's smelter near Garfield, Utah. In 1972 the State of Arizona requested that the Western Area Occupational Health Laboratory investigate environmental conditions in the copper smelting industry in Arizona and consequently detailed surveys were conducted in three smelters. Thus a considerable body of environmental data was available from five smelters processing ores varying in composition and operating in different climatic conditions. However, before a report could be prepared, which would give a general description of environmental conditions in the copper smeltering industry, it seemed necessary to collect additional information from the remaining smelters to ascertain if the pattern of environmental contamination in them was similar to that found in the smelters already studied. Accordingly, preliminary type industrial hygiene surveys were conducted in eight smelters during 1972-73. A detailed survey was also conducted in the White Pine, Michigan smelter, which processes some copper oxide ores, to determine if environmental conditions were markedly different from those in smelters processing only copper sulfide ores.

This report summarizes and presents the determinations of the environmental surveys to provide a broad view of conditions in the industry as a whole, identifying areas in which there are potential health problems.

COPPER ORES AND THE SMELTING PROCESS

Copper occurs in nature as either oxide or sulfide ore (Table 2) or as native copper, with the sulfide ores being the predominant form mined and processed in the United States. Sulfide ores consist basically of a mixture of copper and iron sulfides, valuable trace metals, and a siliceous gangue of no economic value. Some of the common trace elements usually found in copper ore are: arsenic, lead, zinc, cadmium, selenium, molybdenum, gold, and silver.

Little copper ore is treated directly. The sulfide ores usually contain less than 1% copper and, consequently, are usually subjected to a flotation process which produces a concentrate containing from 15 to 30% copper (Table 3). This concentrate is supplied to the smelter, either directly or as a calcine produced by roasting. Smelting is essentially the application of sufficient heat to the copper ore or copper concentrate to cause by fusion the conversion of the gangue into a slag of little value and at the same time to concentrate the copper and other valuable constituents of the ore into a high grade material. The general term "smelting" may be considered to cover the successive operations of roasting, reverberatory smelting, converting, and fire refining.

Roasting, though still used in a few U.S. smelters, is now bypassed in many. The object of roasting is to partially eliminate the sulfur, which is accomplished by heating the metal sulfides in the presence of air to form sulfur dioxide and metallic oxides. All of the excess sulfur in the concentrates is eliminated except that amount necessary to form copper sulfide and iron sulfide in the subsequent smelting operations. The temperature must be sufficiently high to produce a reaction between the oxygen in the air and the excess sulfur, but not so high as to cause fusion of the concentrates. If the particles being roasted were heated to the melting point, protective layers would form as a result of fusion and retard the oxidizing action. In some plants the old roasters are operated at a much lower temperature and used as dryers to control the water content of the concentrate.

The next step in the smelting process is to melt the concentrate or calcine in a reverberatory furnace at a temperature of about 2800°F. The feed and fuel are kept separate and heating is accomplished by radiation from the roof and side wall of the furnace rather than by direct contact with the hot gases. The flame and hot gases guided by a horizontal roof pass over the ore. The gases are then usually directed through a waste heat boiler to recover some of the energy which would otherwise be lost. Although the reverberatory furnace is primarily a melting furnace, some concentration of the copper occurs. The addition of a siliceous flux aids in concentrating the iron into a valueless slag, which is skimmed from the surface of the bath. The copper remains as "matte" at a concentration of about 30-70%. The matte is essentially a mixture of copper sulfide and iron sulfide in varying proportions. All the sulfur in excess of these compounds is expelled in the off-gas as SO_2.

The matte is transferred from the reverberatory furnace to a converter furnace where the iron and sulfur are removed by oxidation. This oxidation is accomplished by forcing streams of air through the molten mass. Again a siliceous flux is added to aid in forming an iron oxide slag which is returned to the reverberatory furnace for reprocessing. Further blowing after removal of the slag produces "blister copper", which is usually 95-98% copper.

The blister copper is further refined in a gas fired, fire refining furnace. A slag is formed consisting of oxides of iron, magnesium, aluminum, and silica. The copper oxide is reduced to metallic copper forming a molten mass of 99+% copper which is usually further refined electrolytically.

SAMPLING AND ANALYTICAL PROCEDURES

Sulfur Dioxide:

Three procedures were used at various times to determine SO_2 concentrations.

1. Indicator tubes were used where an immediate estimate of the SO_2 concentration was required. This information was not used to determine SO_2 exposure, but to make judgements on the relative levels of SO_2 in various areas of the smelter; and as an aid in locating sampling equipment.
2. Air samples of 0.5 to 2 hours duration were collected with midget impingers and were analyzed at the plant site by the West-Gaeke method. (See Appendix, p. 21) This procedure provided a value representing the average concentration of SO_2 during the sampling period. Repeated samples were taken at nearly continual intervals over relatively long periods of time (usually 8-24 hours). In this way a number of short duration values can be used to determine the average concentration in an area over a given shift or day. These data can also be used to determine variability of exposure and to estimate 8-hour time-weighted average exposures if work practices are known and can then be combined with data obtained by the hydrogen peroxide method.
3. The hydrogen peroxide sampling procedure (see Appendix, p. 31) involves drawing air through midget impingers filled with a solution

of hydrogen peroxide and attached to sequential samplers located at strategic sites. The sequential samplers were adjusted to give a continuous series of individual 2-hour average measurements over a 24-hour period. The hydrogen peroxide method is not specific for SO_2 whereas the West-Gaeke method is. However, prior experience showed that serious interferences would not be encountered and no significant error introduced by the presence of SO_3. The hydrogen peroxide method is more suited for sampling over a long period of time, because of the stability of the chemicals involved. The analytical procedures for the West-Gaeke method and hydrogen peroxide methods of SO_2 determinations are presented in the Appendix.

Arsenic:

Arsenic samples were collected on 0.8 μm pore size membrane filters with personal air sampling pumps or sequential samplers. The samples were wet-ashed in nitric acid and then analyzed by atomic absorption.[6] Urine samples were analyzed for arsenic by the silver diethyldithiocarbamate method.[7]

Trace Metals:

The samples for trace metals were collected on 0.8 μm pore size membrane filters with personal air sampling pumps or sequential samplers. After being wet-ashed in nitric acid[6], the concentrations of trace metals, principally lead, cadmium, copper, and zinc, were determined simultaneously on the same filters by atomic absorption. Urine samples were analyzed for lead and cadmium by the APDC-MIBK (ammonium pyerolodino dithiocarbamate-methyl iso-butyl ketone) complexation-extraction and atomic absorption method.[6] Samples for copper were ashed in nitric acid and then analyzed by atomic absorption.[6] Urine samples analyzed for zinc were fed directly into the atomic absorption spectrophotometer.[6]

RESULTS AND DISCUSSIONS

General Discussion:

The initial studies of copper smelters in Montana, Utah, and Arizona, indicated that those areas found to have high atmospheric levels of SO_2 also contained high atmospheric concentrations of arsenic and trace metals. It was also apparent that certain areas of the smelters were consistently higher in levels of air contaminants and other areas were consistently lower. On the basis of these findings it was decided that smelters could be catagorized into four distinct areas: (1) reverberatory furnace charge floors; (2) other areas around the reverberatory furnaces, particularly the matte tapping and slag skimming areas; (3) the converter aisle and areas around the converter furnaces; and (4) anode casting areas. One of the primary purposes of the preliminary surveys of the eight smelters in 1972 and 1973 was to determine if a pattern of relative concentrations of atmospheric contaminants was consistent throughout the industry. This consistency was found to be generally true and, therefore, the results are presented and discussed on the basis of these four areas. An exception was made for the urine samples where the utility, general labor, and maintenance people were considered as a separate group. This is necessary as these employees may not be confined to a specific area within a smelter.

Sulfur Dioxide:

The results of the sulfur dioxide sampling (excluding indicator tube samples) are presented in Table 4. These results were derived by calculating time-weighted averages over the total sampling time for the pertinent area for each smelter, and combining these values into an industry-wide mean for the area. It should be emphasized that these are <u>industry-wide averages</u>

and do not necessarily reflect the concentrations that would be found in any one smelter. They also do not reflect peak values nor are they 8-hour time-weighted averages. They are area averages, and reflect atmospheric concentrations that might be found over a long period of time throughout the copper smelting industry. The indicator tube samples were excluded because they represented instantaneous samples and are not suitable for averaging. Further uncertainty of the meaning of these values, relative to potential health effects, is introduced by the variable fraction of the SO_2 which is adsorbed on nuclei. Amdur[4] has shown the marked potentiation of the biological effects of SO_2 by aerosols, and unpublished data collected by Holaday and Burton[12] demonstrated that a measurable fraction of the SO_2 in one copper smelter was adsorbed on particles.

These data clearly show that the charge floors of the reverberatory furnaces have the highest concentrations of SO_2; potentially, these areas pose the most serious problems. Atmospheric concentrations were found to be lower in the other three areas, and generally similar throughout the industry with a notable exception in the anode casting area of one smelter. This exception is worth discussion as it illustrates the extreme variability which can occur in short-term SO_2 concentrations.

The anode casting area in most smelters is relatively free of SO_2. In one smelter the average value was abnormally high as a result of six samples taken on a day when a strong wind was blowing from the furnace areas toward the anode casting area. These six samples all exceeded 5 ppm, with one value of 219 ppm. Twelve other samples obtained on different days were all below 5 ppm with an average approaching the industry average value of 1.3 ppm. This experience emphasizes the extreme variability of sulfur dioxide concentrations at any place in a smelter and points out the uncertainties involved in using averages of short-term samples collected over limited periods to estimate the degree and extent of health hazards due to sulfur dioxide. From the viewpoint of irritation, however, the short-duration higher-level exposures are more significant than time-weighted averages.

In most smelters the use of respirators* is essential on charge floors of reverberatory furnaces, in the green feed galleries, tripper decks above these furnaces, or any area above the furnaces. In these areas the SO_2 concentrations varied from non-detectable levels to many hundreds of parts per million. It was not unusual for personnel working in these areas to wear respirators continuously without regard to the concentration of SO_2. Concentrations of SO_2 were particularly high during matte tapping as the gases liberated during the operation tended to rise up onto the galleries above the furnace. In distinction men working below on the main floors surrounding the furnaces were not exposed to a great deal of these gases. Most of these men, however, do wear some form of respirator protection when they are actually tapping or skimming. In the converter aisle the workers who would normally be at a high risk are the crane operators, but in all smelters today cleaned air is supplied to the crane cabs. Limited samples taken in crane cabs indicated that SO_2 concentrations were uniformally low, averaging much less than 1 ppm. Moderate levels of SO_2 were found along the converter aisles and around the converter furnaces, but the job requirements of the workers in these areas

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*Because of the irritating properties of sulfur dioxide only those respirators are used which have been found by the employees to afford effective protection. These may be canister respirators containing charcoal and a filter to remove particulates or a cartridge containing charcoal and material to remove acid gases.

apparently obviates long term exposures to concentrations exceeding 5 ppm. As mentioned above, workers in the anode casting area are normally exposed to relatively low concentrations of sulfur dioxide.

It was observed in a large number of smelters, that when air concentrations exceeded the current OSHA standard of 5 ppm, men tended to put on respirators. Employees were seldom seen working in areas where the SO_2 concentration exceeded about 10 ppm who were not wearing some form of respiratory protection.

Arsenic:

Arsenic concentrations were determined using area samples only (Table 5). Initial investigations indicated that airborne concentrations of arsenic would be low relative to the current OSHA standard and since all other information is lost when a filter is analyzed for arsenic, it was decided to use the personal samples for the trace metals. It should be kept in mind that while the air concentrations for arsenic and trace metals, other than copper, are consistently low and well below those specified by current regulations that these data are averages for the entire industry and in no way reflect the average for a particular smelter nor the exposure of a given workman doing a specific job in a smelter. While the conditions in the majority of smelters are accurately reflected in these data, concentrations probably could be found at times in certain smelters which would not comply with existing regulations.

A recent NIOSH criteria document[9] recommends a standard of 0.05 mg As/M^3 of air for a 40-hour work week time-weighted average exposure, a value one-tenth of the current OSHA standard. The recommendation is based on the implication of arsenic as an occupational carcinogen. This value (0.05 mg As/M^3) is not considered "safe" but would "significantly reduce the incidence of arsenic-induced cancer". Although none of the industry-wide averaged presented in Table 5 exceed 0.05 mg As/M^3 the level of some individual samples did. In a recent survey of a smelter processing ore containing higher than average amounts of arsenic, nearly half of the samples had levels in excess of the NIOSH recommendation. Also, exposure to SO_2 and benzo(a)pyrene has been reported by Kuschner[5] to produce lung cancer in rats. This raises the possibility that the biolgical interaction of a lung irritant, such as SO_2, and arsenic might induce carcinogenisis. All of these considerations, then, indicate that a potential for arsenic-induced cancers may exist in some copper smelters.

Trace Metals:

The results of the sample analyses for trace metals are presented in Tables 5 and 6. Concentrations of lead in both the area and personal samples were consistent and well below the OSHA standard of 0.2 mg/M^3 and the NIOSH recommended standard of 0.15 mg/M^3. Lead concentrations appeared to be uniform throughout the smelters with the exception of anode casting areas. Concentrations are shown for zinc and also for zinc oxide. The zinc oxide values were calculated from those found for zinc and may not truly reflect the amount of zinc oxide in the industry as it is possible that the zinc occurs in other than the oxide form. In particular it is probable that a large proportion of zinc might have been in the sulfide form. In any case, the total amount of material present is well below the current standard of 5 mg/M^3. The concentrations of cadmium were also found to be uniformally and consistently low throughout the smelters and in no area did these values approach the standards of 0.1 mg/M^3 for cadmium fume or 0.2 mg/M^3 for cadmium dust. Levels of molybdenum in all cases were found to be insignificant.

Copper:

It is apparent from Tables 5 and 6 that in many plant areas atmospheric concentrations of copper exceed the existing OSHA standards of 0.1 mg/M^3 for copper fume and 1.0 mg/M^3 for copper dust. Data from individual smelters indicate that this is a true industry-wide occurrence. On some of the personal samples, values as high as 30 to 40 mg Cu/M^3 were observed, yet at no time during our study did we receive complaints of the symptoms that would be expected in cases of classic metal fume fever or copper poisoning. This may be because copper oxide or metallic copper are the chemical forms associated with metal fume fever while in copper smelters the majority of the airborne copper is probably present as an insoluble copper sulfide.

It is difficult in a smelter to differentiate between fume and dust, but an attempt was made to obtain some information on the composition of the aerosol. At one smelter two pairs of samples were taken on a reverberatory furnace charge floor. In each pair there was a gross sample collected in the usual manner and a sample obtained by drawing air through a miniture cyclone to remove the essentially "non-respirable" material.* In each case, the cyclone removed better than 99% of the total material collected. This indicates that most of the copper was in the form of large "non-respirable" particles.

A more recent survey conducted in another smelter extensively examined the matter of "respirability". Pairs of personal, breathing zone, approximately 8-hour time-weighted average, samples were obtained from converter furnace and crane aisle employees. One sample was gross dust and the other was a "respirable" sample obtained by preceeding the filter with a cyclone. Twenty-three pairs

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*"Non-respirable" material is defined in this paper as that material which does not pass through a miniture cyclone. Refer to Chapter 8 of Reference 8 in the Bibliography.

of samples were analyzed for cadmium, lead, zinc, and copper; and 14 pairs, for arsenic. The results are presented in Table 8. The ratios and percentages in the Table are the averages for all of the sample pairs. The individual deviations from these averages were not extreme.

The data show that whereas about 25-50% of arsenic, cadmium, lead, and zinc dust was "non-respirable", nearly 94% of the copper dust was included in the "non-respirable" portion. This phenomenon does not appear unusual if the melting and boiling points of the elements involved are examined (Table 9). It is obvious that, within the temperature range at which copper is smelted (about 1300-1500°C), arsenic fume would be readily formed; cadmium and zinc would boil; a high vapor pressure of lead would exist; and the vapor pressure of the copper would be relatively low. Most of the copper collected in the converter department area probably was copper sulfide dust from other areas of the smelter. It is highly doubtful that the airborne arsenic originated in the converter area.

There is little evidence to suggest that there was much copper fume in this particular smelter during the time of the investigation. Fume would have constituted about 6% of the total airborne copper if the assumption is made that the entire "respirable fraction" was fume. The average for the "respirable" samples was 0.03 mg/M^3 with only one sample exceeding the Occupational Safety and Health Administration standard of 0.1 mg/M3 for copper fume. The average gross concentrations was 0.52 mg/M3 of copper.

Urine Concentrations:

The results of the urine sampling are given in Table 7. The normal and harmful exposure limits were determined by a review of existing literature on the toxicity of the various elements. These limits may vary according to source, but appear to represent the best information available at this time. These data indicate that, in the U.S. copper smelting industry as a whole, the exposure to these elements is quite low as most of the values are well within the normal limits or well below harmful exposure limits. Little biological significance can be given to the urine copper values reported. They are included for informational purposes only and for future reference should some significance eventually be attached to urine copper values.

CONCLUSIONS

The environmental surveys included in this report confirmed that relatively high atmospheric concentrations of SO_2 exist in all smelters. The concentrations are extremely variable both in location and time. Respirators are widely used throughout the industry and, therefore, an attempt to estimate individual exposures from the data collected is impossible.

Atmospheric concentrations of trace elements other than arsenic are consistently and uniformally low throughout the industry, although isolated problems may exist in specific jobs in some smelters.

Arsenic does not appear to be an industry-wide problem in regard to the usual acute effects except possibly in those operations which involve handling flue dust. The potential for arsenic-induced cancers may exist in the industry, possibly potentiated by the relatively high atmospheric concentrations of SO_2.

Epidemiological studies would be required to evaluate the nature and extent of any health effects which might occur from exposures to the environment in copper smelters.

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APPENDIX

TABLE 1. PRIMARY COPPER SMELTERS IN THE UNITED STATES

American Smelting and Refining Company
- El Paso, Texas
- Hayden, Arizona
- Tacoma, Washington

The Anaconda Company
- Anaconda, Montana

Cities Service Corporation
- Copperhill, Tennessee

Inspiration Consolidated Copper Company
- Inspiration, Arizona

Kennecott Copper Corporation
- Garfield, Utah
- Hayden, Arizona
- Hurley, New Mexico
- McGill, Nevada

Magma Copper Company
- San Manuel, Arizona

Phelps-Dodge Corporation
- Ajo, Arizona
- Douglas, Arizona
- Morenci, Arizona

White Pine Copper Company
- White Pine, Michigan

TABLE 2. COPPER ORES

OXIDES

Malachite	$CuCO_3.Cu(OH)_2$
Azurite	$2CuCO_3\cdot(CuOH)_2$
Cuprite	Cu_2O
Atacamite	$CuCl_2$
Brochantite	$CuSO_4\cdot 3Cu(OH)_2$

SULPHIDES

Chalcocite	Cu_2S
Chalcopyrite	$Cu_2S\cdot Fe_2S_3$
Covellite	CuS
Bornite	$FeS\cdot 2Cu_2S\cdot CuS$

TABLE 3. RANGE OF CONCENTRATE ANALYSIS

ELEMENT	%
Cu	16 - 32
As	0.001 - 6.7
Pb	0.003 - 1.3
Zn	0.004 - 2.2
Cd	0.001 - 0.04
Mo	0.1 - 0.5

TABLE 4. SULPHUR DIOXIDE CONCENTRATIONS*

AREA SAMPLES

Area	Concentration ppm
Reverberatory Furnace Charging Deck	13.2
Reverberatory Furnace Operators Deck	4.4
Convertor	4.0
Anode Casting	1.3
Current OSHA Standard	5.0
NIOSH Recommended Standard[10]	2.0

*Industry-wide, not representative of any one location.

TABLE 5. CONCENTRATIONS IN AIR. AREA SAMPLING*

Area	mg/M^3						
	Pb	Zn	ZnO (Calculated)	Cu (dust & fume)	As	Cd (dust & fume)	Mo (Total)
Reverberatory Furnace Charging Deck	0.07	0.07	0.09	1.1	0.04	0.005	0.014
Reverberatory Furnace Operators Deck	0.06	0.12	0.15	2.3	0.02	0.012	0.015
Converter Aisle	0.05	0.05	0.06	0.22	0.01	0.003	0.004
Anode Casting	0.01	<0.01	<0.01	0.13	<0.01	0.001	No Data
Current OSHA Standard	0.20	--	5	dust 1.0 fume 0.1	0.5	dust 0.2 fume 0.1	soluble 5 insoluble 15
NIOSH Recommended Standard	0.15[11]	--	--	--	0.05	--	--

*Industry-wide, not representative of any one location.

TABLE 6. CONCENTRATIONS IN AIR. PERSONAL SAMPLING*

Area	mg/M^3					
	Pb	Zn	ZnO (calculated)	Cu (dust & fume)	Cd (dust & fume)	Mo (Total)
Reverberatory Furnace Charging Deck	0.07	0.12	0.15	3.4	0.005	0.003
Reverberatory Furnace Operators Deck	0.07	0.07	0.09	1.3	0.006	0.03
Converter	0.03	0.04	0.05	0.11	0.004	No Data
Anode Casting	0.01	0.01	0.01	0.07	<0.001	No Data
Current OSHA Standard	0.20	--	5	dust 1.0 fume 0.1	dust 0.2 fume 0.1	soluble 5 insoluble 15
NIOSH Recommended Standard	0.15[11]	--	--	--	--	--

*Industry-wide, not representative of any one location.

TABLE 7. CONCENTRATIONS IN URINE*

ELEMENT	Concentration in μgm/L Average	Highest Value	No. Samples
Pb	35	120	278
Cd	2	7	272
Cu	79	1145	206
As	23	170	156
Zn	624	2900	247

TABLE 8. ANALYSIS OF RESPIRABILITY OF ARSENIC AND METAL DUSTS IN ONE U.S. SMELTER

	As	Cd	Pb	Zn	Cu
Average Ratio of Total Dust Collected to Respirable Fraction	1.33	2.02	1.92	1.68	16.5
Average Percent Respirable	75.2	49.5	52.1	59.5	6.1

TABLE 9. MELTING AND BOILING POINTS

Element	Melting Point (°C)	Boiling Point (°C)
Arsenic	Sublimates	—
Cadmium	321	767
Lead	327	1620
Zinc	419	907
Copper	1083	2310

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*Industry-wide, not representative of any one location.

WEST-GAEKE METHOD FOR DETERMINATION OF SULFUR DIOXIDE IN THE ATMOSPHERE (PARAROSANILINE METHOD)

1. PRINCIPLE AND APPLICABILITY OF METHOD

1.1 Sulfur dioxide is absorbed from air in a solution of potassium tetrachloromercurate (TCM). A dichlorosulfitomercurate complex, which resists oxidation by the oxygen in the air, is formed.[1,2] Once formed, this complex is stable to strong oxidants (e.g., ozone, oxides of nitrogen).

1.2 The complex is reacted with pararosanile and formaldehyde to form intensely colored pararosaniline methyl sulfonic acid.[3] The absorbance of the solution is measured spectrophotometrically.

2. RANGE AND SENSITIVITY

2.1 Concentrations of sulfur dioxide in the range of 25 to 1000 $\mu g/M^3$ (0.01 to 0.40 ppm) can be measured under the conditions given. One can extrapolate to concentrations below 25 $\mu g/m^3$ by sampling larger volumes of air, but only if the absorption efficiency of the particular system is first determined. Higher concentrations can be analyzed by using smaller gas samples, a larger collection volume, or a suitable aliquot of the collected sample.

2.2 The lower limit of detection of sulfur dioxide in 10 ml TCM is 0.75 μg (based on twice the standard deviation) representing a concentration of 25 $\mu g/m^3$ SO_2 (0.01 ppm) in an air sample of 30 liters.

2.3 Beer's Law is followed through the working range from 0.03 to 1.0 absorbance units (0.8 to 27 μg of sulfite ion in 25 ml final solution computed as SO_2).

3. INTERFERENCES

3.1 The effects of the principle known interferences have been minimized or eliminated. Interferences by oxides of nitrogen are eliminated by sulfamic acid,[4,5] ozone by time-delay,[6] and heavy metals by EDTA (ethylenediaminetra-acetic acid disodium salt) and phosphoric acid.[4,6] At least 60 μg Fe(III), 10 μg Mn(II), and 10 μg Cr(III) in 10 ml absorbing reagent can be tolerated in the procedure. No significant interference was found with 10 μg Cu(II) and 22 μg V(V).

4. PRECISION, ACCURACY, AND STABILITY

4.1 Relative standard deviation at the 95% confidence level is 4.6% for the analytical procedure using standard samples.[5]

4.2 After sample collection the solutions are relatively stable. At 22°C losses of sulfur dioxide occur at the rate of 1% per day. When samples are stored at 5°C for 30 days, no detectable losses of sulfur dioxide occur. The presence of EDTA enhances the stability of SO_2 in solution, and the rate of decay is independent of the concentration of SO_2.[7]

5. APPARATUS

5.1 Sampling

5.1.1 Absorber - Absorbers normally used in air pollution sampling are acceptable for concentrations above 25 $\mu g/m^3$ (0.01 ppm). An all-glass midget impinger, is recommended for 30-min. samples.

5.1.2 Pump - Capable of maintaining an air pressure differential greater than 0.7 atmosphere at the desired flow rate.

5.1.3 Air Flowmeter or Volume Meter - Capable of measuring air flow within ± 2%. A wet or dry gas meter, with manometer, or a specially calibrated rotameter, is satisfactory. A 22-gauge hypodermic needle 1 in. long may be used as a critical orifice to give a flow of about 1 liter/min. if it has first been calibrated in the system. Use a membrane filter to protect the needle.

5.2 Analysis

5.2.1 Spectrophotometer - Suitable for measurement of absorbance at 548 nm with an effective spectral band of less than 15 nm. Reagent blank problems may occur with spectrophotometers having greater spectral band width. The wavelength calibration of the instrument should be verified. If Transmittance is measured, this can be converted to absorbance:

$$A = \log_{10} (I/T)$$

6. REAGENTS

6.1 Sampling

6.1.1 Distilled water - Must be free from oxidants.

6.1.2 Absorbing Reagent [0.04 M Potassium Tetrachloromercurate (TCM)] - Dissolve 10.86 g mercuric chloride, 0.066 g EDTA (Ethylenediaminetetraacetic acid disodium salt), and 6.0 g potassium chloride in water and bring to mark in a 1000-ml volumetric flask. (Caution: highly poisonous. If spilled on skin, flush off with water immediately). The pH of this reagent should be approximately 4.0, but it has been shown that there is no appreciable difference in collection efficiency over the range of pH 5 to pH 3.[7] The absorbing reagent is normally stable for 6 months. If a precipitate forms, discard the reagent.

6.2 Analysis

6.2.1 Sulfamic Acid (0.6%) - Dissolve 0.6 g sulfamic acid in 100 ml distilled water. Prepare fresh daily.

6.2.2 Formaldehyde (0.2%) - Dilute 5 ml formaldehyde solution (36-38%) to 1000 ml with distilled water. Prepare daily.

6.2.3 Stock Iodine Solution (0.1 N) - Place 12.7 g iodine in a 250 ml beaker; add 40 g potassium iodide and 25 ml water. Stir until all is dissolved, then dilute to 1000 ml with distilled water.

6.2.4 Iodine Solution (0.01 N) - Prepare approximately 0.01 N iodine solution by diluting 50 ml of stock solution to 500 ml with distilled water.

6.2.5 Starch Indicator Solution - Triturate 0.4 g soluble starch and 0.002 g mercuric iodide (preservative) with a little water, and add the paste slowly to 200 ml boiling water. Continue boiling until the solution is clear; cool, and transfer to a glass-stoppered bottle.

6.2.6 Stock Sodium Thiosulfate Solution (0.1 N) - Prepare a stock solution by dissolving 25 g sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) in 1000 ml freshly boiled, cooled, distilled water and add 0.1 g sodium carbonate to the solution. Allow the solution to stand 1 day before standardizing. To standardize, accurately weigh, to the nearest 0.1 mg, 1.5 g primary standard potassium iodate dried at 180°C and dilute to volume in a 500 ml volumetric flask. To a 500-ml iodine flask, pipet 50 ml of iodate solution. Add 2 g potassium iodide and 10 ml of 1 N hydrochloric acid. Stopper the flask. After 5 minutes, titrate with stock thiosulfate solution to a pale yellow. Add 5 ml starch indicator solution and complete the titration. Calculate the normality of the stock solution:

$$N = \frac{W}{M} \times 2.80$$

N = normality of stock thiosulfate solution
M - volume of thiosulfate required, ml
W - weight of potassium iodate, grams

$$2.80 = \frac{10^3 \text{ (conversion of g to mg) x 0.1 (fraction iodate used)}}{\text{35.67 equivalent weight of potassium iodate}}$$

6.2.7 Sodium Thiosulfate Titrant (0.01 N) - Dilute 100 ml of the stock thiosulfate solution to 1000 ml with freshly boiled distilled water.

Normality = Normality of Stock Solution X 0.100.

6.2.8 Standardized Sulfite Solution For Preparation of Working Sulfite-TCM Solution - Dissolve 0.30 g sodium metabisulfite ($Na_2S_2O_5$) or 0.40 g sodium sulfite (Na_2SO_3) in 500 ml of recently boiled, cooled, distilled water. (Sulfite solution is unstable; it is therefore important to use water of the highest purity to minimize this instability). This solution contains the equivalent of 320 to 400 µg/ml of SO_2. The actual concentration of the solution is determined by adding excess iodine and back-titrating with standard sodium thiosulfate solution. To back-titrate, pipet 50 ml of the 0.01 N iodine into each of two 500 ml iodine flasks (A and B). To flask A (blank) add 25 ml distilled water, and to flask B (sample) pipet 25 ml sulfite solution. Stopper the flasks and allow to react for 5 min. Prepare the working sulfite-TCM Solution (6.2.9) at the same time iodine solution is added to the flasks. By means of a buret containing standardized 0.01 N thiosulfate, titrate each flask in turn to a pale yellow. Then add 5 ml starch solution and continue the titration until the blue color disappears.

6.2.9 Working Sulfite-TCM Solution - Pipet accurately 2 ml of the standard solution into a 100 ml volumetric flask and bring to mark with 0.04 M TCM. Calculate the concentration of sulfur dioxide in the working solution:

$$\mu g\ SO_2/ml = \frac{(A-B)\ (N)\ (32,000)}{25} \times 0.02$$

A = volume thiosulfate for blank, ml
B = volume thiosulfate for sample, ml
N = normality of thiosulfate titrant
32,000 = milliequivalent wt., µg
25 = volume standard sulfite solution, ml
0.02 = dilution factor

This solution is stable for 30 days if kept at 5°C. (refrigerator). If not kept at 5°C., prepare daily.

6.2.10 Purified Pararosaniline Stock Solution (0.2% nominal)

6.2.10.1 Dye Specifications - The pararosaniline dye must meet the following performance specifications: (1) the dye must have a wavelength of maximum absorbance at 540 nm when assayed in a buffered solution of 0.1 M sodium acetate-acetic acid; (2) the absorbance of the reagent blank, which is temperature-sensitive (0.015 absorbance unit/°C), should not exceed 0.170 absorbance unit at 22°C with a 1-cm optical path length, when the blank is prepared according to the prescribed analytical procedure and to the specified concentration of the dye; (3) the calibration curve (Section 8.2.1) should have a slope of 0.030 ± 0.002 absorbance units/µg SO_2 at this path length when the dye is pure and the sulfite solution is properly standardized.

6.2.10.2 Preparation of Stock Solution - A specially purified (99-100% pure) solution of pararosaniline, which meets the above specifications, is commercially available in the required 0.20% concentration (Harleco*). If this cannot be obtained, the stock solution may be prepared by dissolving 0.200 g of the purified dye in 100 ml of 1 N hydrochloric acid in a 100 ml glass stoppered graduated cylinder. (See Scaringelli, et. at.[4] for the purification and assay procedures).

6.2.11 Pararosaniline Reagent - To a 250 ml volumetric flask; add 20 ml stock pararosaniline solution. Add an additional 0.2 ml stock solution for each per cent the stock assays below 100%. Then add 25 ml 3 M phosphoric acid and dilute to volume with distilled water. This reagent is stable for at least 9 months.

7. PROCEDURE

7.1 Sampling - Procedures are described for short term (30 min.) and for long term (24 hours) sampling. One can select different combinations of sampling rate and time to meet special needs. Fixing sample volume at 30 liters maintains linearity between absorbance and concentration over this dynamic range.

7.1.1 30-Minute Sampling - Insert a midget impinger into the sampling system, Figure 1. Add 10 ml TCM solution to the impinger. Collect sample at 1 liter/min. for 30 min. Shield the absorbing reagent from direct sunlight during and after sampling by covering the impinger with aluminum foil, to prevent deterioration. Record the actual volume of air by multiplying the flow rate by the time in min. Remove and stopper the impinger. If the sample must be stored for more than a day before analysis, keep it at 5°C in a refrigerator (see 4.2).

7.1.2 24-Hour Sampling - Place 15-20 ml TCM solution in a midget impinger or 50 ml in a larger impinger and collect the sample at 0.2 liter/min. For 24 hours. Make sure no entrainment of solution results with the impinger. During collection and storage protect from direct sunlight. Record the total volume of sample by multiplying the flow rate by the time in min. If storage is necessary, refrigerate at 5°C (see 4.2).

7.2 Analysis

7.2.1 Sample Preparation - After collection, if a precipitate is observed in the sample, remove it by centrifugation.

7.2.1.1 30 Minute Sample - Transfer the sample quantitatively to a 25 ml volumetric flask; use about 5 ml distilled water for rinsing. Delay analyses for 20 min. to allow any ozone to decompose.

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*Hartmen-Leddon, 60th & Woodland Ave., Philadelphia, Pennsylvania 19143

7.2.1.2 24 Hour Sample - Dilute the entire sample to 25 ml for the midget impinger or 50 ml for the larger impinger, with absorbing solution. Pipet one-tenth of the sample into a 25-ml volumetric flask for chemical analyses. Bring volume to 10 ml with absorbing reagent. Delay analyses for 20 min.

7.2.2 Determination - For each set of determinations prepare a reagent blank by adding 10 ml unexposed TCM solution to a 25-ml volumetric flask. Prepare a control solution by adding 2 ml of working sulfite-TCM solution and 8 ml TCM solution to a 25-ml volumetric flask. To each flask containing either sample, control solution or reagent blank, add 1 ml 0.6% sulfamic acid and allow to react 10 min. to destroy the nitrite from oxides of nitrogen. Accurately pipet in 2 ml 0.2% formaldehyde solution, then 5 ml pararosaniline solution. Start a laboratory timer that has been set for 30 minutes. Bring all flasks to volume with freshly boiled and cooled distilled water and mix thoroughly. After 30 min. and before 60 min., determine the absorbances of the sample, reagent blank and the control solution at 548 nm using 1-cm optical path length cells. Use distilled water, not the reagent blank, as the reference. (NOTE! This is important because of the color sensitivity of the reagent blank to temperature changes which can be induced in the cell compartment of a spectrophotometer.) Do not allow the colored solution to stand in the absorbance cells, because a film of dye may be deposited. Clean cells with alcohol after use. If the temperature of the determinations does not differ by more than 2°C from the calibration temperature (8.2), the reagent blank should be within 0.03 absorbance unit of the y-intercept of the calibration curve (8.2). If the reagent blank differs by more than 0.03 absorbance unit, from that found in the calibration curve, prepare a new curve.

7.2.3 Absorbance Range - If the absorbance of the sample solution ranges between 1.0 and 2.0, the sample can be diluted 1:1 with a portion of the reagent blank and read within a few minutes. Solutions with higher absorbance can be diluted up to six-fold with the reagent blank in order to obtain on-scale readings within 10% of the true absorbance value.

8. CALIBRATION AND EFFICIENCIES

8.1 Flowmeters and Hypodermic Needle - Calibrate flowmeters and hypodermic needle[8] against a calibrated wet test meter.

8.2 Calibration Curves

8.2.1 Procedure with Sulfite Solution - Accurately pipet graduated amounts of the working sulfite-TCM solution (such as 0, 0.5, 1, 2, 3, and 4 ml) into a series of 25-ml volumetric flasks. Add sufficient TCM solution to each flask to bring the volume to approximately 10 ml. Then add the remaining reagents as described in 7.2.2. For maximum precision use a constant-temperature bath. The temperature of calibration must be maintained within ± 1°C and in the range of 20 to 30°C. The temperature of calibration and the temperature of analysis must be within 2 degrees. Plot the absorbance against the total concentration in μg SO_2 for the corresponding solution. The total μg SO_2 in solution equals the concentration of the standard (Section 6.2.9) in μg SO_2/ml times the ml sulfite solution added (μg SO_2 = μg/ml SO_2 x ml added). A linear relationship should be obtained, and the y-intercept should be within 0.02 absorbance unit of the zero standard absorbance. For maximum precision determine the line of best fit using regression analysis by the method of least squares. Under these conditions the plot need be determined only once to determine the calibration factor (reciprocal of the slope of the line). (See Section 6.2.10.1 for specifications on the slope of the calibration curve). This calibration factor can be used for calculating results provided there are not radical changes in temperature or pH. At least one control sample containing a known concentration of SO_2 for each series of determinations, is recommended to insure the reliability of this factor.

8.2.2 Procedure with SO_2 Gas - See Appendices.

8.3 Sampling Efficiency - Collection efficiency is above 98%; efficiency may fall off, however, at concentrations below 25 μg/m³.[9,10]

9. CALCULATIONS

9.1 Conversion of Volume - Convert the volume of air sampled to the volume at standard conditions of 25°C, 760 mm Hg:

$$V_s = V \times \frac{P}{760} \times \frac{298}{(t + 273)}$$

V_s = volume of air at 25°C and 760 mm Hg
V = volume of air sampled, liters
P = barometric pressure, mm Hg
t = temperature of air sample, °C

Ordinarily, the correction for pressure is slight and may be neglected.

9.2 Sulfur Dioxide Concentration - Compute the concentration of sulfur dioxide in the sample by the following formula:

$$SO_2,\ \mu g/m^3 = \frac{(A - A_o)(10^3)(B)}{V_s}$$

A = sample absorbance
A_o = reagent blank absorbance,
10^3 = conversion of liters to cubic meters
V_s = the sample volume corrected to 25°C and 760 mm Hg., liters

$$B = \frac{1}{\text{Slope of calibration curve, absorbance units}/\mu g} = \text{calibration factor, } \mu g/\text{absorbance unit}$$

9.2.1 Conversion of $\mu g/m^3$ to ppm - If desired, the concentration of sulfur dioxide may be calculated as ppm SO_2 at standard conditions as follows:

$$\text{ppm } SO_2 - \mu g\ SO_2/m^3 \times 3.82 \times 10^{-4}$$

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HYDROGEN PEROXIDE METHOD FOR DETERMINATION OF SULFUR DIOXIDE IN THE ATMOSPHERE

1. PRINCIPLE OF THE METHOD

1.1 Sulfur dioxide in the air is absorbed and oxidized in 0.3 normal hydrogen peroxide reagent.

1.2 The pH of the sample solution is adjusted with dilute perchloric acid. After isopropyl alcohol is added bringing the alcohol concentration to approximately 80% by volume, the resulting solution is titrated with 0.005 M barium perchlorate using Thorin as the indicator. There is a sharp change from yellow to pink at the end point.

2. RANGE AND SENSITIVITY

This method is sensitive to 0.1 mg sulfur dioxide per cubic meter assuming a 100 liter air sample. This would correspond to approximately 0.25 ppm SO_2 in air. The upper limit is the amount of SO_2 absorbed in the hydrogen peroxide reagent and is at least 5 mg.

3. INTERFERENCES

3.1 Soluble particulate sulfates, and sulfuric acid in the air sample would give erroneously high sulfur dioxide values. However, these can be eliminated by placing a 0.8μ cellulose filter upstream of the impinger in the sampling train.

3.2 Metal ion interferences can be eliminated by either the use of a pre-filter or, alternatively, by passing the solution through an ion exchange column.

3.3 Concentrations of phosphate ions greater than the sulfate ion concentration cause appreciable interference. Phosphate can be removed by precipitation with magnesium carbonate. The use of a prefilter should also remove phosphates.

4. PRECISION AND ACCURACY

At 2.5 ppm the accuracy is 5% with a relative standard deviation of 4%. At 25 ppm accuracy and relative standard deviation can be improved to about 1%.

5. ADVANTAGES AND DISADVANTAGES

5.1 The samples are easily collected and conveniently shipped to the laboratory for analysis in glass vials.

5.2 The sulfuric acid formed is stable and nonvolatile, making this manner of collection of SO_2 desirable.

5.3 The analysis is relatively rapid and simple.

6. APPARATUS

6.1 Absorber - Glass midget impingers or fritted bubblers.

6.2 Personal sampling pump with flow meter capable of sampling at a rate of 1.8 lpm.

6.3 Millipore 0.8μ cellulose AA filters and cassettes.

6.4 Necessary glassware

6.5 Buret - a buret of 10 milliliter capacity graduated in 0.05 milliliter subdivisions.

6.6 Daylight fluorescent lamp aids in identifying the end point.

6.7 Ion exchange Resin - Dowex 50x8, 20-50 mesh, hydrogen form Ion exchange columns may be constructed using glass burets or tubing. A column with an inside diameter of 8 mm and 7 inches of resin has a capacity of approximately 25 milliequivalents.

7. REAGENTS

7.1 Alcohol - Isopropanol, reagent grade.

7.2 Barium Perchlorate, 0.005 M. Dissolve 2.0 grams of barium perchlorate trihydrate in 200 ml of water and add 800 ml of isopropanol. Adjust apparent pH to about 3.5 with perchloric acid. Standardize against 0.005 M H_2SO_4.

7.3 Thorin - Prepare a 0.1% to 0.2% solution in distilled water.

7.4 Standard Sulfate Solution - Prepare a 0.005 M solution of H_2SO_4 and standardize by titration with 0.02 N sodium hydroxide or dissolve 0.7393 g anhydrous Na_2SO_4 in distilled water and dilute to one liter (1 ml = 0.5 mg SO). The sodium is removed by passage of the standard through the ion exchange column.

7.5 Hydrochloric Acid, 4 N - Add 300 ml conc. HCl to 600 ml of distilled water. Needed only to regenerate the column if the ion exchange procedure is used.

7.6 Absorbing Solution - Hydrogen Peroxide, 0.3 N - Dilute 17 ml of 30% H_2O_2 solution to one liter with distilled water.

7.7 Perchloric Acid, 1.8% - Dilute 25 ml of reagent grade perchloric acid (70-72%) to one liter with distilled water.

8. PROCEDURE

8.1 Cleaning of Equipment - The glassware should be chemically clean. Wash in detergent, and rinse with tap water and distilled water.

8.2 Collection and Shipping of Samples

8.2.1 Sulfur dioxide is absorbed in 15 ml of hydrogen peroxide absorbing solution in an impinger equipped with a 0.8µ filter upstream.

8.2.2 Air is drawn through the impinger by means of a personnel sampling pump at the rate of 1.8 liters per minute. A minimum of 100 liters of air should be sampled. If SO_2 concentrations greater than 100 milligrams per cubic meter of air are expected, smaller air volumes should be collected.

8.2.3 For every ten samples, one blank impinger containing H_2O_2 should be provided.

8.2.4 After the sample solutions from the impingers are transferred into vials, the vials are shipped in a suitable container to prevent damage in transit.

8.3 Ion Exchange Procedure (Used to purify Standard Sulfate Solution and for samples only when filters were not used in front of the impinger.)

8.3.1 When about two thirds of the capacity of the resin has been exhausted (deterioration in sharpness of the end point), regenerate the resin by passing 30 ml of 4 N hydrochloric acid through the column. After thorough washing with distilled water, the column is ready for use.

8.3.2 Since small volumes of sample solution are passed through the ion exchange column, care must be taken not to dilute the sample with distilled water that remains on the resin. One way this can be accomplished is by blowing some air through the resin with a squeeze bulb to remove most of the distilled water from the ion exchange resin. One or two milliliters of sample is passed through the column and is discarded after air is again blown through the resin. The remainder of the sample is then passed through the ion exchange column, and an aliquot is titrated according to the general procedure (Section 8.4.3).

8.3.3 The column is flushed with distilled water between samples to prevent contamination from the previous sample.

8.4 Analysis of Samples

8.4.1 Measure the volume of the sample solution or dilute it to a given volume.

8.4.2 Although all samples may be passed through the ion exchange column, it is necessary to do so only when the metal concentration exceeds that of the sulfate. The ion exchange procedure is detailed in Section 8.3. Use of a prefilter upstream from the impinger should remove most metal ions and thus eliminate this entire step, however.

8.4.3 To a 10 ml aliquot, add 40 ml isopropanol. Adjust the pH if necessary to between 2.5 and 4.0 with perchloric acid. Add 1 - 3 drops Thorin indicator and titrate with barium perchlorate, taking the change from yellow or yellow-orange to pink as the end point.

8.4.4 Analyze the standard and absorbing solution blank in the same manner.

9. CALIBRATION AND STANDARDS

9.1 The barium perchlorate solution is standardized by titrating a 5 ml aliquot of the standardized H_2SO_4 (0.005 M) to the end point with Thorin as indicator. The molarity of the solution is calculated as follows:

$$M_{Ba[ClO_4]2} = \frac{ml_{H_2SO_4} \times M_{H_2\ SO_4}}{ml_{Ba(ClO_4)2}}$$

Periodic checks of the molarity of the $Ba(ClO_4)_2$ solution should be run following this same procedure.

9.2 If anhydrous sodium sulfate is used to standardize the barium perchlorate, it must first be ion exchanged since sodium obscures the end point. A five milliliter aliquot of the 0.5 mg/ml sulfate solution is ample for standardization.

10. CALCULATIONS

The analytical results are computed on the basis of the following reactions:

$$SO_2 + H_2O_2 \rightarrow H_2SO_4$$

$$H_2SO_4 + Ba(ClO_4)_2 \quad BaSO_4 \downarrow + 2\ HClO_4$$

$$\frac{\text{mg } SO_2}{M_3} = \frac{ml_2 \times M_{Ba(ClO_4)_2} \times MW_{SO_2}}{Vm^3} \times \frac{V}{V_{aliq}}$$

ml_2 = ml of $Ba(ClO_4)_2$ solution needed to titrate the sample aliquot minus the blank value.

MW_{SO_2} = molecular weight of SO_2 = 64

Vm^3 = Volume of air sampled in cubic meters

V_{aliq} = Volume of sample aliquot used for the titration in ml

V = Original volume of sample in impinger in ml

OR

$$\text{ppm } SO_2 \text{ by volume} = \frac{ml_s \times M_{Ba(ClO_4)_2} \times 24{,}450}{V_1} \times \frac{V}{V_{aliq}}$$

V_1 = Volume of air sampled in liters at 25°C

24,450 = ml/mole that ideal gas occupies at 25°C

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