Investigation of an Air Sampling and Analytical Method for METHYL ETHYL KETONE PEROXIDE

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I. Introduction

Methyl Ethyl Ketone Peroxide (MEKO) has been demonstrated to cause both acute and subchronic toxicity in various mammalian species (1), leading to a recommendation by the American Conference of Government Industrial Hygienists of a 0.2 ppm time-weighted average maximum exposure level. The chemical is used mainly as a free radical initiator for various polymerization processes. Since the amount of initiator necessary for most polymerization processes is quite small, it follows that the amount in the workplace air is likely to be very small in comparison to, for example, monomer concentration. The chemical structure, containing the peroxide functionality, implies certain special problems with sample stability. In particular, those things which are known to catalyze peroxide decomposition were thought likely to constitute potential sources of error in the analysis. In this group are heat, light and heavy metal ions.

Prior to the initiation of this research a method was developed under contract for NIOSH (2) based on an earlier analytical method (3,4) which seemed to have the requisite sensitivity. It was subsequently examined in more detail by the Utah Biomedical Test Laboratory (UBTL) under contract to NIOSH (5). The UBTL findings were that the lower limits claimed by the original contractors were too low by about an order of magnitude, but that the analytical method was otherwise workable. The method as devised by the original contractor (2) consisted of: (a) collection of the sample in a dimethyl phthalate bubbler, (b) removal of an aliquot of the collected sample and (c) spectrophotometric analysis of the colored product formed by heating with diphenylcarbohydrazide. No collection efficiency or sample stability data were produced (2). There were, however, anecdotal reports that the method did not "work". The basis for such assertions turned out to be that no detectable amounts of MEKO were found in areas where the chemical was in use. A more detailed look at the existing method seemed to be a good starting point for this project. The method which resulted from these studies is found in Appendix A.

II. Stability

As glass surfaces contain acidic OH groups bound to silicon atoms, the surface is, in effect, a cation exchanger. As was previously noted, heavy metal ions are well-known as catalysts for peroxide decomposition, and they might well be present exchanged onto the glass surfaces. All glassware, unless otherwise noted was soaked overnight in Nochromix®, rinsed with distilled deionized water, dried in an oven and finally silanized by treatment with dichlorodimethylsilane. The surface is thereby transformed into one containing $(CH_3)_2Si$ groups. After use, glassware was washed with acetone, detergent, distilled deionized water and dried in an oven. This treatment gave relatively repeatable results, as judged by the constancy of the slope of the standard curve, over a 5- to 6-month period. After this time the slope declined severely. When the glassware was subjected to the original cleaning regimen and resilanized, the slope of the standard curve returned to its previous level.

The effects of chemical agents were investigated by adding various chemicals to known concentrations of MEKO in dimethyl phthalate (DMP) and observing the disappearance over time of MEKO as compared to controls (no chemicals added). The chemicals chosen were: styrene, cobalt naphthenate, 2,2'-bipyridine and 3-tert-butyl-4-hydroxy-5-methylphenylsulfide (BHMPS). The first compound was chosen because it typifies a reactive monomer which is likely to be collected along with the MEKO. The second compound is typical of the "accelerators" used to start the free radical chain reaction. The third compound, bipyridine, is a large organic ligand and was used to complex the cobalt, thus markedly increasing the solubility of the metal ion in the DMP solution. The fourth addend was a free radical inhibitor, tested to see whether its use would retard the decomposition of the peroxide. Results of these tests are presented in Table 1. The experimental values were obtained by adding the amounts and kinds of the above compounds to 5 mL of an MEKO solution of approximately 25 ug/mL. These tubes along with a control containing only 5 mL of the same MEKO solution were allowed to sit (covered with aluminum foil) for the time period indicated and then analyzed. The conclusion from these data is that, while solutions of MEKO in the presence of certain of the test compounds are stable for various times at various temperatures, only at freezer temperature were samples containing styrene stable for a week, independent of soluble cobalt concentration. Since these are likely co-contaminants in the industrial setting, this was chosen as the condition for later storage tests.

III. Study of Analytical Parameters

In order to understand the effects of the important parameters on the color produced in the analytical reaction, a two-level factorial experiment was set up. The parameters studied and the levels of each were as follows:

parameter	upper level	lower level
temperature	90 °C	70 °C
time	15 min	3 min
oxygen	present	absent

All levels were done in duplicate.

The dependent variable was the absorbance of the analyzed solution. Results showed the following main effects:

temperature - positive effect
time " "
oxygen " "

The largest effect noted was the temperature-time interaction which was negative (i.e. longer reaction time has a larger effect on reactions run at low temperature than those run at high temperature). The magnitude of the main effects was small, and, given the 10% or so day-to-day variation of the slope of the standard curve, the only significant effect was the temperature-time interaction. This information was used to modify the method by the following reasoning. If one allows the reaction to proceed at a lower temperature for a longer period of time, one should approach the same level of the dependent variable as would be obtained at a higher temperature for a short time. The original method (2,4) calls for heating in a boiling water bath for 3 minutes. The boiling water bath is inconvenient, and, if many samples are to be analyzed and the bath is of limited size, it is hard to maintain temperature during the initial addition of the samples. The time during which the samples are not at boiling water temperature may be, therefore, a significant fraction of the total reaction time. When the reaction bath temperature was lowered to 85°C and the reaction time was 15 minutes, more reproducible results were obtained in terms of variations in the slope of the standard curve from day to day.

IV. Storage Studies

A freezer storage study was planned in which 2 test tubes were to be stored for 1 day, 2 for 1 week, and 6 for 2 weeks. In actual practice it turned out to be 2 for 1 day, 2 for 19 days, and 6 for 21 days. The stored samples consisted of 5 mL of DMP containing 204 ug MEKO. Three standards to bracket the samples were prepared each day samples were analyzed. The concentration of the MEKO remaining in the samples was then determined from that standard curve.

When the standard curve was run to analyze the 1 day samples, the slope of the standard curve was found to be very much lower than that which had been obtained previously. Various changes in reagents, solvents, etc. failed to restore the slope to its previous values. A recleaning and resilanizing of the glassware did, however, accomplish the restoration of the previous values of the slope.

The rest of the storage samples were then run. Results are given in Table 2. Two samples stored for 19 days were 92.9% of the initial concentration. Six samples stored for 21 days were 89.6% of the initial concentration. Thus about 10% was lost on storage for 21 days.

V. Collection Efficiency and Vapor Pressure

Air was pumped through two sets of 2 bubblers at 1 L/min for 4 hours. One of the two sets was silanized. The first bubbler of each set contained 20 mL of a 50.6 ug/mL solution of MEKO in DMP (a 5-mL aliquot therefore contained 253 ug MEKO) and the second contained only 20 mL DMP. All bubblers were wrapped with aluminum foil. After the 4-hour period two 5-mL portions were removed from each bubbler and placed in stoppered test tubes, to which color reagent was added. Solutions were analyzed. Results are given in Table 3.

The absorbance of the experimental samples was compared to a control which consisted of a 5-mL aliquot of the same solution used to fill the bubblers. The results show a) that over a 4-hour period less than 10% of the MEKO was carried over from the front to the back-up bubbler, implying a very low vapor pressure of MEKO, and b) that the concentration of the residual MEKO in the silanized bubbler was somewhat higher than that in the non-silanized one. This piece of data, although admittedly not demonstrating a dramatic difference, led us to suggest that the glassware used to collect samples be silanized.

In a second experiment, a silanized U-tube was spiked with 1 mL of a 0.234 mg/mL solution of MEKO in DMP. Air (240 L), was pumped through the U-tube at 1 L/min into a bubbler containing 15 mL of DMP. The resulting solution in the bubbler was analyzed along with a standard. The solution remaining in the U-tube was washed out with 5 mL DMP into another test tube and analyzed. The absorbance of the solution in the bubbler was below the level of the lowest analytically quantifiable level. This fact was a further indication of the low vapor pressure of MEKO. If all the MEKO had been vaporized the concentration of the solution in the bubbler would have been 15.6 ug/mL, and the 5-mL aliquot used for analysis would have contained 78 ug of MEKO. Therefore, if as much as 1/3 of the MEKO had been volatilized and trapped in the bubbler, it would have been detected.

In the next experiment, impingers were used instead of bubblers. The front impinger was filled with 20 mL of a 54.9 ug/mL solution of MEKO in DMP, while the back impinger contained 20 mL DMP. Air was drawn through the set of impingers at 1 L/min for 4 hours. The impingers were wrapped with aluminum foil. The same procedure as before was followed for each reaction and analysis. The average absorbance of the solution from the back-up impinger was 0.143, not significantly different from a blank. The average absorbance of the MEKO solution from the first impinger was 93.5% of the control. The second time the experiment was run the average absorbance of the first impinger was 90.1% of the control. The absorbance of the back-up impinger solution was .118, indistinguishable from the blank. Again, at most about 10% of the MEKO present in the first impinger was lost. This may be due to volatilization of a small fraction of the MEKO or to decomposition, or both.

VI. Study of collection of MEKO on teflon filters.

Since collecting air samples in impingers can be awkward, an attempt was made to test the use of filter cassettes for this purpose. Initially 100 uL of DMP was pipetted onto teflon filters. The DMP dissolved the cassette and caused it to stick to the filter. An equal amount of a solution of 10 uL DMP in 5 mL methyl ethyl ketone (MEK) was spiked onto the filter. This solution did not cause a sticking problem.

Tests were then done by spiking filters in cassettes with 100 uL of a 1.33 mg MEKO/mL in MEK solution (containing 1% DMP) while drawing in air at 1 L/min for 5 min. The cassettes were capped and set aside covered with foil. The filters were then removed from the cassettes and placed in screw-capped vials to which 5 mL DMP was added. The vials were placed in an ultrasonic bath for 15 min after which the solution was transferred to reaction test tubes. Two controls were prepared by adding 100 uL of the stock solution (1.33 mg MEKO/mL in MEK) to 5 mL DMP in test tubes. These controls contained the same weight of MEKO but had not contacted the filters.

All test tubes were analyzed alike. The solutions from the spiked filter showed an absorbance of about one half that of the controls. Results are presented in Table 4.

In a further experiment six filters were spiked with 133 ug MEKO (100 uL of a 1.33 mg MEKO/mL in MEK solution). Air was pulled through 4 of them in cassettes at 1 L/min for 2 hours. The remaining 2 filters were placed in cassettes then covered with foil and set aside. Two standards were prepared by adding 100 uL of the 1.33 mg MEKO/mL in MEK solution to 5 mL DMP. Before analysis 100 uL MEK was added to two of the extracts from the group of four filters that had air pumped through them. The no air filters showed absorbances 65% and 61% of the standard. The two solutions to which MEK was added were 45% and 43% of the standards, whereas the remaining two solutions had absorbances similar to the blank. From these results it was determined that the presence of methyl ethyl ketone was a positive interference, and that pulling air through the MEKO-containing filters led to the disappearance of the peroxide, or alternatively that MEKO was not stable on the filters. In any case, collection on filters was rejected.

VI. Effect of ketones on absorbance.

In doing the previous experiments with filters a definite enhancement of absorbance was observed arising from the presence of methyl ethyl ketone. It was decided to examine this phenomenon further. Four test tubes containing 5 mL DMP each were spiked in duplicate with 25 uL and 100 uL of a ketone. Also four test tubes containing 5 mL of an MEKO solution (19 ug/mL) were spiked in duplicate as above with 25 uL and 100 uL of the same ketone. Ketones tested were methyl ethyl ketone (used as is and filtered through alumina and activated charcoal to remove any peroxides), acetone, cyclohexanone and 3-methyl-2-butanone. All the ketones except acetone showed a positive interference.

VII. Precision and Accuracy

A. Standardization of MEKO

To determine the actual % MEKO in the technical grade material as it comes from the supplier, an iodine liberation method involving titration with sodium thiosulfate was used. The method used was an adaptation of the Hercules Method I. (6) The initial standardization of sodium thiosulfate was accomplished using a procedure in NIOSH Manual of Analytical Methods. (7) The standardized 0.1N sodium thiosulfate solution was then used to standardize the MEKO solution.

The method called for refluxing the MEKO and sodium iodide in acidified isopropyl alcohol for 15 min. From this procedure the average % MEKO was 58.48%, relative standard deviation (R.S.D.) 0.62% (n = 2). The method was repeated without refluxing but setting aside the flasks in a dark place for 15 min. The average % MEKO was 58.68%, R.S.D. 0.0% (n = 2). This value is only slightly less than the nominal 60% MEKO as supplied.

B Precision

Four trials were run of standards made at 3 levels close to 100, 170, and 210 ug/10 mL at a reaction temperature at 85 $\pm$ 5°C for 15 min. Slopes from these experiments plus two earlier trials averaged 0.425 AU/ug with an R.S.D. of 9.8%. The time period over which this average was compiled was six months. The precision of measurement of replicates done the same day at the 100 ug/10 mL level was 1.5% R.S.D. Assuming a pump error of 5% the total uncertainty in the method is then:

$$\text{Overall R.S.D.} = \sqrt{(.05)^2 + (.015)^2 + (.098)^2} = 0.111$$

This is a "worst case" calculation. If the standards and samples are run on the same day then the overall R.S.D. would be 5.22%. The uncertainty in the intercept for a three-point standard curve is substantial. However, this component of variance is only important at or near the intercept. Since this method specifies the value of the absorbance must be twice that of the intercept, the non-inclusion of that uncertainty seems reasonable. Results are presented in Table 5.

VIII. References

1. Floyd, E. P. and Stokinger, H. E. Toxicity Studies of Certain Organic Peroxides and Hydroperoxides, Am. Ind. Hyg. Assoc. J. 19: 205-212 (1958).

2. Final Report NIOSH Contract 210-75-0030. May 1978.

3. Stamm, J., Evidence of Decomposition in Oils and Fats, Analyst, 51:416 (1926).

4. Hamm, D. L., Hammond, E. G., Parvanah, V. and Snyder, H. E. The Determination of Peroxides by the Stamm Method, J. Amer. Oil Chem. Soc., 42:920 (1965).

5. Allen, B., Utah Biomedical Test Laboratory, Memorandum to Kupel, R. NIOSH, Feb. 23, 1977.

6. Mair, R. D. and Graupner, A. J. Determination of Organic Peroxides by Iodine Liberation Procedures, Anal. Chem. 36:194(1964).

7. NIOSH Manual of Analytical Methods, Second Ed., Vol. 1., U. S. DHEW, NIOSH, Cincinnati, Ohio 45226, 1977, Method No. P&CAM 209, 7.6 to 7.9.

TABLE 1

Effects of Various Chemicals on the Disappearance of MEKO[a]

Storage Temperature	Storage Time (days)	Additives[b]	Absorbance of Analyzed Solution
Ambient	2	none	0.635
"	2	C&B	0.521
"	2	B	0.575
"	2	S	0.598
"	3	none	0.550
"	3	C	0.505
"	3	C+B+P	0.093
"	3	C+P	0.151
refrigerator	2	none	0.675
"	2	C+S	0.691
"	2	B+C+S	0.698
"	7	none	0.589
"	7	B+C+S	0.518
freezer	7	none	0.651
"	7	C+S	0.664
"	7	B+C+S	0.661

a. concentration range of MEKO 113-139 ug/10 mL; all results are averages of duplicate runs

b. B = BHMPS (see text for full name), 50 uL of 1% solution in DMP
C = cobalt naphthenate, 50 uL of a 0.6% suspension in DMP
S = styrene, 10 uL
P = bipyridine, 100 uL of a 10% solution in DMP

TABLE 2

Storage Study[a]

Storage Period (days)	Amount MEKO taken (ug)	Amount MEKO found (ug)	Recovery (%)
19	204	189	92.6
19	204	190	93.1
average ± standard deviation.			92.9 ± 3.6%
21	204	183	89.7
21	204	182	89.2
21	204	184	90.2
21	204	181	88.7
21	204	183	89.7
21	204	184	90.2
average ± standard deviation.			89.6 ± 0.65%

a. All samples stored in freezer

TABLE 3

Collection Efficiency and Vapor Pressure Experiments[a]

Collection Devices		Loading ug/20 mL MEKO	Absorbance Experimental	Absorbance Control	Experimental as % of control
Bubbler[b]	Front	1012	0.865	0.905	95.6
	Back		0.091[c]		
Bubbler	Front	1012	0.838	0.905	92.6
	Back		0.093[c]		
Impinger	Front	1098	1.020	1.091	93.5
	Back		0.143[c]		
Impinger	Front	816	0.840	0.932	90.1
	Back		0.118[c]		

a. all experiments run for 4 hours

b. Silanized bubbler

c. Not significantly different from blank

TABLE 4

Filter Studies[a]

Matrix	Air Volume (L)	n	Absorbance
teflon filter	5	1	0.516
teflon filter[b]	5	1	0.366
control	0		1.096
teflon filter	0	2	0.632
teflon filter	120	2	0.189
teflon filter[c]	120	2	0.446
control	0	2	1.007

a. loading 133 ug MEKO

b. part of filter stuck to cassette

c. 100 uL MEK added to filter extract before analysis

TABLE 5

Precision Experiments

I	Slopes:	(AU/ug)	0.0407
		"	0.0463
		"	0.0441
		"	0.0473
		"	0.0362
		"	0.0406
		Average	0.0425 ± 9.8% R.S.D.

II Replicate samples done same day:

Nominal concentration	- 10 ug/mL
Absorbances -	0.567
	0.584
	0.567
	0.565
Average	0.571 ± 1.5% R.S.D.

APPENDIX A

METHYL ETHYL KETONE PEROXIDE

Measurements Research Branch

Analytical Method

Analyte:	Methyl ethyl ketone peroxide (MEKO)	Method No:	P&CAM 331
Matrix:	Air	Range:	0.31 - 3.1 mg/m^3 for a 250-L air sample
Procedure:	Absorption in dimethyl phthalate in impinger, colorimetric analysis.	Precision:	0.052
Date Issued:	8/29/80		
Date Revised:		Classification:	E (Proposed)

1. Synopsis

   1.1 Methyl ethyl ketone peroxide is collected in a midget impinger containing 15 mL of dimethyl phthalate.

   1.2 A 5-mL aliquot of the resulting solution is transferred to a stoppered, silanized test tube and diphenylcarbohydrazide color reagent is added. Heating produces a violet color.

   1.3 Spectrophotometric analysis is made at 565 nm and quantitation of the analyte is then accomplished by comparison to known standards.

2. Working Range, Sensitivity and Detection Limit

   2.1 The probable range of the method is 0.31 to 3.1 mg/m^3.

   2.2 The lowest analytically quantifiable level for this method was arbitrarily defined as the level corresponding to twice the absorbance of the blank or about 25 µg/10 mL in the analyzed solution. The upper limit is set by the fact that the absorbance vs. concentration curve is linear only to about 250 µg/10 mL in the analyzed solution. Performing a volumetric dilution can extend the range in 2.1 upward. However, the sample as analyzed must fall between twice the blank and 250 µg/10 mL to be usable.

3. Interferences

3.1 An interference with this analytical procedure could arise from other peroxides or any strong oxidant.

3.2 Most ketones will exhibit positive interference at high levels, except acetone which does not affect the analysis.

3.3 Substances which catalyze the decomposition of peroxide may cause a significant decrease in the measurement. In particular, the presence of metal ions adsorbed on the glassware may catalyze this decomposition.

3.4 Since it is not possible to compensate for these interferences, care should be taken to preclude their presence where possible, for example, by carefully cleaning and silanizing all glassware. If the presence of ketones other than acetone is suspected, a separate sample should be taken and analyzed for ketones.

4. Precision and Accuracy

4.1 The overall precision of the method was 0.052 relative standard deviation. This figure was arrived at by including variances associated with pump error, and random error of analysis. Day-to-day changes in the slope of the standard curve were significant. If samples and standards are not run the same day, the relative standard deviation will be about twice as large.

4.2 Samples stored at freezer temperature showed a 10% loss over 21 days.

4.3 The accuracy of the analytical method was assessed by relating the MEKO content of the commercial material to primary standard $K_2Cr_2O_7$.

5. Advantages and Disadvantages

5.1 Collected samples are analyzed by a rapid instrumental method.

5.2 No sample elution or desorption is required because the sample is collected in a liquid medium.

5.3 A disadvantage of the method is the awkwardness of using midget impingers for collecting samples.

5.4 A disadvantage is relative non-specificity of the diphenylcarbohydrazide color reaction.

5.5 A disadvantage is the special care that must be taken in the conditioning of the glassware and in the storage of the samples.

6. Apparatus

6.1 Midget impingers, glass 25-mL, silanized.

6.2 Personal sampling pump. A calibrated personal sampling pump whose flow rate can be determined to an accuracy of 5%. Each personal sampling pump must be calibrated with a representative impinger and splash-over trap in the line to minimize errors associated with uncertainties in the volume sampled.

6.3 Test tubes, 18 mm X 150 mm, with glass stoppers, silanized.

6.4 Water bath, capable of holding a constant temperature of 85 $\pm$ 5 ^{o}C.

6.5 Cold water bath, 25 $\pm$ 5 ^{o}C.

6.6 Spectrophotometer, capable of reading at 565 nm.

6.7 Matched glass cells or cuvettes, 1-cm path length.

6.8 Stopwatch

6.9 Assorted laboratory glassware, all silanized. Pipets, Class A, volumetric transfer, various sizes; volumetric flasks, beakers, burette, graduated cylinders, Erlenmeyer flasks.

6.10 Shipping vials, silanized, 20 mL, Teflon-lined caps.

6.11 Cold chest, insulated, dry-ice cooled.

7. Reagents

7.1 Dimethyl phthalate, reagent grade.

7.2 Glacial acetic acid, reagent grade.

7.3 Diphenylcarbohydrazide, reagent grade.

7.3.1 Diphenylcarbohydrazide solution. Dissolve 0.25 g $\pm$ .01 g of diphenylcarbohydrazide in dimethyl phthalate and dilute to 100 mL. This solution is light sensitive and should be prepared in a darkened place fresh each day immediately before using. The rate of solution of diphenylcarbohydrazide is slow and may be speeded up by placing the flask in an ultrasonic bath. Solution should then rest long enough to cool and return to volume.

7.3.2 Color Reagent. Mix 30 mL of the 0.25% diphenylcarbohydrazide solution with 20 mL glacial acetic acid. Prepare fresh immediately before use.

7.4 Methyl ethyl ketone peroxide (MEKO), 60%, Technical Grade

MEKO Stock Solution. Pipet about 10 µL of the nominally 60% MEKO into a 50 mL pre-weighed flask. After accurately weighing the flask plus MEKO fill to volume with dimethyl phthalate. Wrap flask in foil. Working standards of MEKO containing 5 to 50 µg/mL of MEKO in dimethyl phthalate are made from the stock solution.

7.5 Reagents for Standardization of Commercial MEKO.

7.5.1 Starch indicator solution.

7.5.2 Potassium iodide, reagent grade.

7.5.3 Sodium thiosulfate solution, 0.1 N.

7.5.4 Isopropyl alcohol, reagent grade.

7.5.5 Sodium iodide, reagent grade. Sodium iodide solution. Dissolve 20 g sodium iodide in 100 mL isopropanol.

7.6 Sodium bisulfite.

7.7 Nochromix .

7.8 5% dichlorodimethylsilane in toluene.

8. Procedure

8.1 Cleaning of Equipment.

8.1.1 Initially all glassware should be washed in detergent, rinsed with tap water, then deionized water and then soaked overnight in a Nochromix® solution (made with concentrated sulfuric acid and a packet of Nochromix®). After the Nochromix® soak, glassware is rinsed with deionized water, dried in an oven and cooled to room temperature. Glassware is then silanized by filling with a 5% dichlorodimethylsilane in toluene solution (Sylon CT or equivalent) for 1 min. followed by a toluene, then a methanol rinse,then dried. After use, glassware should be rinsed with methanol, detergent washed, thoroughly rinsed with tap water followed by 4-5 rinsings with deionized water and then rinsed with methanol and oven-dried at 120 °C overnight after each use. Allow glassware to cool down to room temperature before using.

8.1.2 Cleaning of Matched Spectrophotometric Cuvettes. The cuvettes, previously matched, should be kept scrupulously clean and free of scratches, fingerprints, smudges and evaporated film residues and should be cleaned by detergent, followed by deionized water rinses, and then acetone.

8.2 Collection and Shipping of Samples

8.2.1 Pipet 15 mL of dimethyl phthalate into each impinger. Wrap in aluminum foil.

8.2.2 Connect a foil-wrapped impinger to an empty impinger positioned between the exit arm of the first impinger and a personal sampling pump using a short piece of flexible tubing. Connect the empty impinger to the sampling pump using flexible tubing. The air being sampled should not pass through any tubing or other equipment before entering the first impinger.

8.2.3 Turn on the pump to begin sample collection. Care should be taken to measure the sampling time as accurately as possible. Record atmospheric pressure and temperature. If pressure reading is not available, record the elevation. The sample should be taken at a flow rate of 1.7 L/min. A sample size of at least 240 liters is recommended (approximately 2.5 hrs sampling time).

8.2.4 After sampling, the contents of each impinger should be quantitatively transferred to silanized, aluminum foil-wrapped vials and tightly sealed. They should be placed in the cold chest as quickly as feasible.

8.2.5 Whenever possible, hand delivery of the samples packed in dry ice is recommended. Otherwise, special cases containing dry ice should be used to ship the samples. Mark "Fragile" on the container.

8.2.6 A "blank" impinger should be handled in the same way as the other samples (fill, seal and transport) except that no air is sampled through the impinger.

8.2.7 Samples of the bulk liquid which contain the MEKO should be submitted to the laboratory in exactly the same manner as the samples (i.e. in silanized, aluminum foil-wrapped vials in the cold chest).

8.2.8 Storage. After receipt in the laboratory, the vials are stored in the freezer. (Note: Analysis should be completed as soon as possible. Samples stored as long as three weeks have shown 10% loss of sample.)

8.3 Analysis of Samples

8.3.1 Transfer in duplicate exactly 5.0 mL of each sample into a silanized test tube.

8.3.2 Pipet 5.0 mL of the diphenylcarbohydrazide color reagent into each of the tubes, stopper and invert several times to mix.

8.3.3 Loosen the stopper and heat the test tubes in a water bath at 85 $\pm$ 5 ^{o}C for 15 minutes.

8.3.4 Cool in a room temperature water bath for exactly 5 minutes.

8.3.5 Zero the spectrophotometer with dimethyl phthalate vs. air.

8.3.6 Read the absorbance of the samples at 565 nm in a spectrophotometer vs. air, when a stable value is obtained.

8.4 Disposal of MEKO solutions: Prepare 250 mL of a saturated aqueous solution of sodium bisulfite in a 1-L beaker. Store in a hood. Add all waste solutions containing MEKO to this beaker. Allow to stand for a week before disposing of the two phase mixture.

9. Calibration and Standardization

9.1 Standardization of commercial MEKO. The 60% MEKO should be standardized initially and weekly thereafter to determine its true concentration.

9.1.1 First standardize the sodium thiosulfate solution, 0.1 N, by following NIOSH Manual of Analytical Methods, Vol. 1, P&CAM 209, paragraphs 7.6 to 7.9 or follow directions in any analytical chemistry text. Alternatively standardized thiosulfate may be purchased from any one of several suppliers.

9.1.2 Weigh out 1 g of the nominally 60% MEKO in a 100 mL volumetric flask. Record weight to nearest mg. Dilute to 100 mL with isopropanol, cover flask with foil.

9.1.3 In a 250-mL iodine flask, place approximately 25 mL isopropyl alcohol. Add 5 mL glacial acetic acid. Then add 10 mL of the 20% sodium iodide in isopropyl alcohol solution to the flask.

9.1.4 Pipet exactly 10 mL of the MEKO solution from 9.1.2 above, into the flask, cover and let stand in the dark for 15 min.

9.1.5 Add 10 mL distilled water immediately before titrating.

9.1.6 Titrate with 0.1 N sodium thiosulfate from a yellow to colorless end point. Record the volume in mL used.

9.1.7 A blank containing all reagents except MEKO also should be titrated in exactly the same way.

9.1.8 Calculation of Weight % MEKO.

$$C_S = \frac{(V_S - V_B)\ 4.405}{W}$$

where:
C_S = % MEKO as the cyclic dimer
V_S = volume of 0.1 N $Na_2S_2O_3$ used to titrate the sample (mL)
V_B = volume of 0.1 N $Na_2S_2O_3$ used to titrate the blank (mL)
W = weight of commercial MEKO used(g)
4.405 = constant containing the milliequivalent weight of MEKO (as the cyclic dimer) and various dilution factors

9.2 Aliquots of the MEKO stock standard (Section 7.4.1) are diluted to prepare the various working standards. Dimethyl phthalate is used as the solvent in preparing all standards. Prepare stock and working standards fresh daily. Wrap the volumetric flasks in aluminum foil.

9.3 Prepare at least 3 standards over the range of expected concentrations.

9.4 Analyze as in Section 8.6.

9.5 The standards and unknowns are treated exactly alike and analyzed during the same time period using the same batch of reagents.

9.6 Construct a calibration curve by plotting absorbance against concentration of MEKO in µg/10 mL of solution. Extrapolate to zero concentration. This is the "blank" value. Any sample whose absorbance is less than twice the "blank" should be reported as less than that level.

10. Calculations

10.1 From the standard curve, find the concentrations of the samples in µg MEKO/10 mL. Convert to air concentrations as follows:

$$C_A = \frac{3(C_f - C_B)}{V_A}$$

where: C_A = air concentration in mg/m^3
C_f = concentration of MEKO in µg/10 mL in the analyzed solution
V_A = volume of air sampled in liters
C_B = concentration of the sample blank (if greater than twice the reagent blank)

10.2 For personal sampling pumps with rotameters only, the following correction should be made:

$$V_A = f \times t \sqrt{\frac{P_1 T_2}{P_2 T_1}}$$

where: V_A = corrected volume
P_1 = atmospheric pressure during pump calibration (mm Hg)
P_2 = atmospheric pressure during sampling (mm Hg)
T_1 = ambient temperature during pump calibration (°K)
T_2 = ambient temperature during sampling (°K)
f = sample flow rate (L/min)
t = sampling time (min)

11. References

11.1 NIOSH Manual of Analytical Methods, Second Ed., Vol. 1, U. S. Dept. HEW, NIOSH, Cincinnati, Ohio 45226, 1977, Method No. P&CAM 209.

11.2 Mair, R. D. and Graupner, A. J., Determination of Organic Peroxides by Iodine Liberation Procedures, Analytical Chemistry, 36, 194 (1964).

11.3 Hamm, D. L., Hammond, E. G., Parvanah, V. and Snyder, H. E., J. Am. Oil Chem. Soc. 42, 920 (1965).

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