

DISMANTLING AN EXHAUST VENTILATION SYSTEM SUSPECTED OF CONTAMINATION WITH PERCHLORATES

Dismantling a laboratory exhaust system contaminated with shock-sensitive perchlorates is a hazardous operation, as evidenced by published and unpublished case histories. The procedures used by one university to reduce the hazards were described by Peter A. Breyse in the Occupational Health Newsletter (15(2 and 3) 1, February–March 1966) published by the Environmental Health Division, Department of Preventive Medicine, School of Medicine, University of Washington. The problem, procedures, and confirmation of perchlorate contamination were reported as follows.

A short time ago, the manager of Maintenance and Operations was requested to dismantle and relocate six laboratory exhaust systems. The possibility of perchloric acid contamination of these systems was considered. An investigation indicated that several laboratories serviced by the exhaust systems were utilizing or had in the past, used perchloric acid for wet ashing of tissues. Furthermore, the exhaust hoods were constructed with sharp corners and cracks, permitting the accumulation of contaminants not readily noticed or easily removed. The ducts were made of ceramic material and contained numerous joints as well as a number of elbows—areas conducive to perchlorate build-up. Organic compounds were also used—to pack the duct joints, as an adhesive for the flexible connectors, and as a sealing compound for the fan.

Recognizing the potential dangers of dismantling these systems, the following procedures were established and successfully carried out.

1. It was deemed desirable to dismantle the systems on the weekend when occupancy would be at a minimum.
2. The entire system was washed for 12 hours, just prior to dismantling, by introducing a fine water spray within the hoods, with the fans operating.
3. The fans were then hosed down.
4. Fan mounting bolts and connectors were carefully removed. Non-sparking tools were and should be used throughout.
5. The fans were immediately removed to the outdoors. As an added precaution during removal the fans were covered with a wet blanket.
6. After all the fans were taken outdoors one fan at a time was placed behind a steel shield for protection during dismantling. This fan was again washed down.
7. Plate bolts were evenly loosened to remove the plate without binding. If a fan puller is necessary, it should be nonsparking.
8. All disassembled parts were washed and cleaned. The gasket material contained on the flanges was scraped off with a wooden scraper.
9. Ordinarily, the ceramic ducts would be removed by breaking them apart with a sledge hammer. In this instance, the ducts were washed down again just prior to and during dismantling. A high speed saw was used to remove the duct work.

One of the flexible connectors and a piece of duct-joint sealing compound were collected and taken to the laboratory for examination. Qualitative analysis by X-ray fluorescence and chemical tests indicated the presence of perchlorates in both samples. While these procedures for dismantling and decontamination seem unduly severe, the uncertainty requires that they be followed.

Heating of perchloric acid should be accomplished within an exhaust system designed for this purpose. The exhaust hood should have smooth surfaces for ease of cleaning. Preferably the exhaust ducts should rise vertically in a straight

line with the exhaust stack extended at least eight feet above the roof line to provide adequate dissipation. Nonabsorbent materials, such as stainless steel, should be utilized throughout the system and all organic sealers and compounds should be omitted. Since there is always the possibility that traces of perchloric acid will react with air-borne substances to form deposits within the system's confines, periodic washing of the entire structure is desirable. For greatest safety electric heating should be utilized with the controls located outside the hood. All spills should be cleaned up immediately and the hood should be posted—PERCHLORIC ACID HOOD, KEEP COMBUSTIBLES OUT.

SUMMARY AND CONCLUSIONS

The use of perchloric acid is becoming increasingly widespread and the properties of both the acid and its derivatives make it likely that the trend will continue. Perchloric acid may be used in safety, provided that its hazardous properties are clearly recognized, the purpose of the acid in a process is fully understood, and measures are taken to avoid known possibilities.

It is, however, clear that no one should attempt to use perchloric acid who is not fully conversant with the chemistry of the material and who has not made a careful appraisal of his operating conditions and techniques.

SAFE WORKING CONDITIONS

When assessing the minimum requirements to insure safe working conditions the following three questions are of importance.

1. Is the work involving the use of perchloric acid likely to be a continuing rather than an occasional and infrequent commitment?
2. Will the use of perchloric acid be accompanied by any form of heating? (Heat of reaction and frictional heat should not be overlooked in this context.)
3. Is it intended to use perchloric acid more concentrated than the 72% azeotrope?

Should the answer to all these questions be "no," then, in the absence of any other contra-indications, relaxation of the normal standards may be considered. If, however, a positive answer is received to any of these questions the working conditions should conform to the recommended standards. Any deviation from these standards should be made only with the agreement of the departmental safety supervisor.

APPENDIX 1—SOME ACCIDENTS INVOLVING PERCHLORIC ACID

1. Explosions may occur when 72% perchloric acid is used to determine chromium in steel, apparently due to the formation of mixtures of perchloric acid vapor and hydrogen. These vapor mixtures can be exploded by the catalytic action of steel particles.¹

2. Two workers are reported to have dried 11,000 samples of alkali-washed hydrocarbon gas with magnesium perchlorate over a period of 7 years without accident. However, one sample containing butyl fluoride caused a purple discoloration of the magnesium perchlorate with the subsequent explosion of the latter.¹

3. A worker using magnesium perchlorate to dry argon reported an explosion and warned that warming and contact with oxidizable substances should be avoided.¹

4. An explosion was reported when anhydrous magnesium perchlorate used in drying unsaturated hydrocarbons was heated to 220°C.¹

5. An explosive reaction takes place between perchloric acid and bismuth or certain of its alloys, especially during electrolytic polishing.^{1,4}

6. Several explosions reported as having occurred during the determination of potassium as the perchlorate are probably attributable to heating in the presence of concentrated perchloric acid and traces of alcohol. An incident in a French laboratory is typical: an experienced worker in the course of a separation of sodium and potassium removed a platinum crucible containing a few decigrams of material and continued the heating on a small gas flame. An explosion pulverized the crucible, a piece of platinum entering the eye of the chemist.⁶

7. A violent explosion took place in an exhaust duct from a laboratory hood in which perchloric acid solution was being fumed over a gas plate. It blew out windows, bulged the exterior walls, lifted the roof, and extensively damaged equipment and supplies. Some time prior to the explosion, the hood had been used for the analysis of miscellaneous materials. The explosion apparently originated in deposits of perchloric acid and organic material in the hood and duct.⁷

8. A chemist was drying alcohol off a small anode over a bunsen burner in a hood reserved for tests involving perchloric acid. An explosion tore the exhaust duct from the hood, bent a portion of the ductwork near the fan, and blew out many panes of window glass.⁷

9. An employee dropped a 7-lb bottle of perchloric acid solution on a concrete floor. The liquid was taken up with sawdust and placed in a covered, metal waste can. Four hours later, a light explosion blew open the hinged cover of the can. A flash fire opened three sprinklers which promptly extinguished the fire.⁷

10. A 7-lb bottle of perchloric acid solution broke while an employee was unpacking a case containing three bottles. The spilled acid instantly set the wood floor on fire, but it was put out quickly with a soda-acid extinguisher.⁷

11. At a malleable iron foundry, perchloric acid had been used for about four years in the laboratory for the determination of the silicon contents of iron samples. A cast iron, wash-sink drain at the bench used for this purpose had corroded and the leaking acid had soaked into the wood flooring, which was later ignited while a lead joint was being poured. This fire was extinguished and part of the wood flooring was removed. Later in the day, at a point slightly removed from the location of the first fire, a similar fire occurred when hot lead was again spilled. This time the fire flashed with explosive violence into the exhaust hood and stack above the work bench. Laboratory equipment and records were wet down extensively, and damaged.

12. A stone table of a fume hood was patched with a glycerin cement and several years later, when the hood was being removed, the table exploded when a workman struck the stone with a chisel. The hood had been used for digestions with perchloric acid and, presumably, acid spills had not been properly cleaned up.⁸

13. A conventional chemical hood normally used for other chemical reactions, including distillation and ashing of organic materials, was also used during the same time for perchloric acid digestion. During a routine ashing procedure, the hot gases went up the 12 in. tubular transit exhaust duct and one of a series of explosions occurred that tore the duct apart at several angles and on the horizontal runs.⁸

14. During routine maintenance involving partial dismantling of the exhaust blower on a perchloric acid ventilating system, a detonation followed a light blow with a hammer on a chisel held against the fan at or near the seal between the rear cover plate and the fan casing. The intensity of the explosion was such that it was heard four miles away and of the three employees in the vicinity, one sustained face lacerations and slight eye injury; the second suffered loss of four fingers on one hand and possible loss of sight in one eye; the third was fatally injured with the 6 in. chisel entering below his left nostril and embedded in the brain.⁸

15. A 6-lb bottle of perchloric acid broke and ran over a fairly large area of wooden laboratory floor. It was cleaned up, but some ran down over wooden joists. Several years later a bottle of sulfuric acid was spilled in this same location and fire broke out immediately in the floor and the joists.⁸

16. A chemist reached for a bottle of perchloric acid stored on a window sill above a steam radiator. The bottle struck the radiator, broke, and the acid flowed over the hot coils. Within a few minutes the wooden floor beneath the radiator burst into flame.⁸

17. An explosion occurred when an attempt was made to destroy benzyl celluloses by boiling with perchloric acid.¹¹

18. An explosion occurred as anhydrous perchloric acid was being prepared via sulfuric acid dehydration and extraction with methylene chloride when a stopper was removed from the separatory flask.¹⁴

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Ralph - Let me know if this was not legible. My original is on yellow so our copier darkened the background. If unreadable, I'll send you hardcopy.

Good Luck,
Ralph

Research and Development Fact Sheet

Controlling Perchloric Acid Fumes

PROBLEM

Most laboratories have an occasional need to use a strong mineral acid such as perchloric acid which generates reactive and corrosive fumes. If perchloric work is done in a fume hood which previously was or later is used for organic materials, an explosive reaction can occur. This fact sheet describes an acceptable method for controlling acid fumes without the use of a perchloric acid fume hood with water wash exhaust system.

DISCUSSION

It is generally agreed that a fume hood that will safely accommodate perchloric acid must have a mechanism to completely water wash all exposed parts. Because of its cost, such a hood may not be available where there is only occasional use of perchloric acid. Consequently, the operation that generates perchloric acid fumes is usually conducted in an existing fume hood which is used for other types of work. Oxidizable materials (such as lint or condensed organic materials) are likely to be present and may cause an explosive reaction on contact with perchloric acid fumes. An explosive reaction can also occur when perchlorate residue is retained in the hood exhaust system and organic material is introduced into the system.

Exhaust ducts are commonly fabricated from galvanized steel, stainless steel, or coated steel. A severe corrosion problem exists when perchloric acid fumes are generated in a hood exhaust system constructed of these materials. The use of corrosion-resistant materials such as plastics or glass are costly and may create other problems requiring special fire protection and fabrication.

SOLUTION

One acceptable method for controlling perchloric acid fumes as they are generated is to use a water-powered aspirator to absorb them. The acid formed is neutralized in a tank containing marble chips before being released as liquid waste. There are three basic types of apparatus which may be used to collect acid fumes. The process generating the fumes determines the most appropriate type of apparatus that should be used.

1. For acid evaporation from a beaker, large flask, dish, or similar container, the apparatus in Figure 1, with a polyethylene aspirator for $\frac{1}{2}$ inch water pipe connection or a standard brass aspirator should be used.

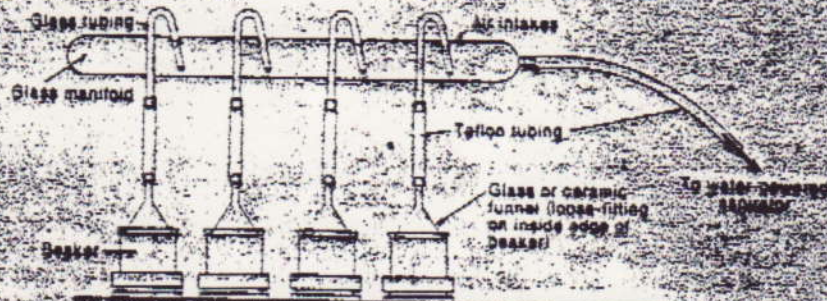


Figure 1

- For Kjeldahl-type digestions and similar type operations, the apparatus in Figure 2, with vacuum applied by means of the water-powered aspirator, should be used.

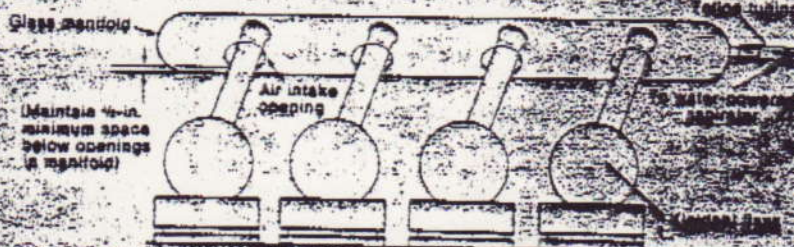


Figure 2

- For reflux of acid used to decarbonize a sample or to dissolve heavy metals the apparatus in Figure 3, should be used. The end of the condenser may be a plain tube or a standard taper joint; it should not be a ball joint or socket.

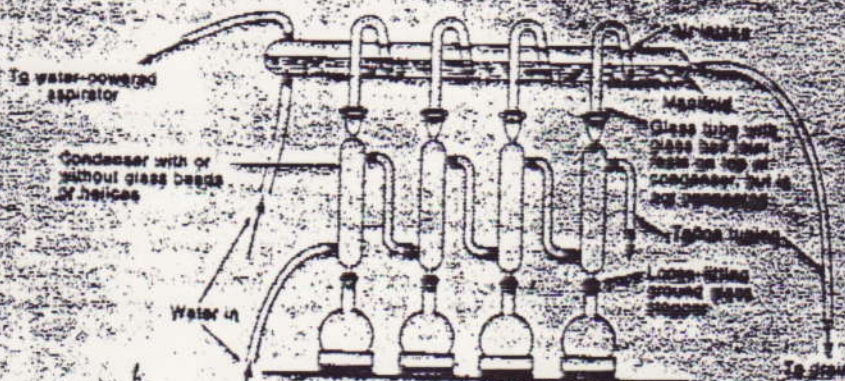


Figure 3

The glass apparatus in these operations should be rinsed free of acid following each use and the tubing connecting the manifold and aspirator should have water drawn through it with the aspirator.

REFERENCE

NSC Data Sheet 655, Recognition and Handling of Peroxidizable Compounds

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