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DETERMINATION OF CHROMIUM COMPOUNDS IN GASEOUS ATMOSPHERES

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4 Claims. (Cl. 23-254)

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This invention relates to the determination of hexavalent chromium in gaseous atmospheres, and more especially to the determination of chromic acid mists in air.

Colorimetric procedures for this purpose are known, and one that has been used is the color reaction between hexavalent chromium and s-diphenylcarbazide (s-DPC). The s-DPC reagents previously used have been subject, however, to the disadvantage that they inherently discolor rapidly, in consequence of which freshly prepared reagents have been necessary. For that reason procedures involving the determination of hexavalent chromium by means of s-DPC have not been adapted to field use, and the necessity for having freshly prepared reagent has likewise militated against use in the laboratory.

A major object of the invention is to provide a method of determining hexavalent chromium in a gaseous atmosphere, and especially chromic acid mists in air, that is simple, reliable, rapid, direct, and adapted particularly to field use, and the practice of which requires no special or technical training.

A further object is to provide a reagent for use in the method provided by the invention that is of simple composition, relatively inexpensive, and exhibits acceptably long useful life.

Still another object is to provide means for determining hexavalent chromium, such as chromic acid mists in air, that is simple, easily prepared and used, and possesses desirably long shelf life.

Other objects will appear from the following description.

The invention is predicated in large part upon our discovery that the disadvantages heretofore encountered in the determination of hexavalent chromium by s-diphenylcarbazide are avoided by the use of a reagent comprising that compound and a solid acid that is non-volatile at ordinary temperature and pressure. In its preferred embodiment the reagent includes also a humectant. Thereby there is provided satisfactory sensitivity, rapidity of determination, the ability to make determinations in the field by non-technical workers, and long reagent life, so that there is no longer need to prepare fresh reagent each time a determination is to be made.

Among the solid acids and acidic reagents that we have found operable are sulfanilic, benzoic, cinnamic and boric acids and potassium bipthalate. However, in the preferred practice of the invention phthalic anhydride is used be-

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cause we find that it confers maximum reagent stability and sensitivity.

For the determination of hexavalent chromium compound in a gaseous atmosphere, for example chromic acid mists in air, we pass the atmosphere to be examined through an absorbent base carrying or impregnated with our new reagent. Such detecting means may be prepared most readily by treatment of an absorbent base with a solution of the reagent in a volatile solvent. The solvent acts purely as a carrier of the reagent, to provide a medium that will penetrate and carry the reagent through the absorbent base and then be volatilized from the base, leaving the reagent distributed through it. The action of the solvent is thus purely physical, and a wide variety of volatile solvents are, of course, applicable. We prefer the lower alcohols, and for most purposes ethanol. Where the reagent is applied to the impregnation of an absorbent material it is preferred to add to the solution a humectant that remains in the base and causes the reagent to be sufficiently moist for rapid reaction between it and the chromium compound.

As in the case of the solvent, the action of the humectant is wholly physical as it does not enter into the color-forming reaction. Instead of glycerine any of the well-known humectants, such as diethylene glycol and triethylene glycol, may be used provided they are neutral and do not have a destructive action upon the absorbent medium.

We have found that an eminently satisfactory reagent is provided by 4 grams of phthalic anhydride and 0.25 gram of s-DPC in 100 cc. of ethanol (95%). To this solution there is added 20 cc. of glycerine as the preferred humectant. This reagent we have found to possess long useful life. For example, filter paper impregnated with it remains without deterioration, when properly stored, for at least 6 months. The stain produced on a white base, such as filter paper, is reddish-violet to purple, and it is stable for at least four hours.

The proportions in which the s-DPC and solid acid are used will depend, at least to some extent, upon the particular solid acid. In general, the lower the content of acid the slower the reaction proceeds, and in the example just given about 1 per cent of phthalic anhydride is about the lowest practical concentration. The content may vary from that amount to saturation. We find that with phthalic anhydride the best results are to be had with solutions containing 0.25 per cent, ± 0.05 per cent, of s-DPC. The s-DPC may vary from about 0.1 to about 0.3 or 0.4 per cent

although below about 0.2 per cent the reaction is delayed and above the upper limit stated filter paper carrying the reagent tends to become colored upon prolonged storage. The concentration of the humectant is not critical provided there is sufficient of it present to maintain sufficient moisture for prompt reaction.

Preferably the reagent is carried by filter paper although a wide variety of other absorbent base materials may be used such, for example, as compressed absorbent cotton, cotton felt, wool felt, cotton cloth of appropriate density, and such inorganic bases as porous filter discs of fused alumina, such as those sold by the Norton Company as "Alundum." The absorbent material is soaked in the reagent solution, after which it is dried to evaporate the solvent. The absorbent base carrying the reagent is then stored until it is to be used. The impregnated material should be kept in tightly stoppered containers having a minimum of free air space, suitably in brown glass jars. Although as stored in this manner the impregnated material has a desirably long life, the life can be prolonged still further by keeping it at a low temperature, e. g., in a refrigerator. Storage in an atmosphere of nitrogen or other inert gas will also increase the shelf life of the impregnated material. Deterioration of the detecting means thus prepared is indicated by an appearance of a strong coloration; the development of a faint coloration is not objectionable.

In practicing the invention using filter paper, or other absorbent base material, carrying the reagent, the atmosphere to be tested is passed through the impregnated absorbent base, as by means of a hand pump. We have found that for many purposes it is desirable to use Eaton and Dikeman filter paper No. 623, of 0.026 inch thickness, which for all practical purposes shows an efficiency of 100 per cent in removing chromium acid mist from air passed through an exposed diameter of 1 inch at rates of 0.25 to 1 C. F. M. A satisfactory field procedure using paper impregnated with the reagent in accordance with the foregoing example is to use a hand pump to force the air or other atmosphere through the impregnated paper, mounted to expose an area about 1 inch in diameter, as described by us in a paper in *Jour. Ind. Hygiene and Toxicology*, vol. 26, p. 316 (1944). When the atmosphere is passed through the impregnated filter paper development of the characteristic color shows the presence of hexavalent chromium. Or, by passing a predetermined, or known, volume of the atmosphere, and comparing the depth of color developed with color standards produced by known concentrations of hexavalent chromium, there is provided rapid, direct quantitative determination of the concentration of the chromium compound in the atmosphere. For many purposes we prefer to accomplish this by 10 strokes of a hand pump that delivers 600 cc. of air per squeeze.

Suitable comparison standards for this purpose may be prepared by matching the stain colors produced by known concentrations of hexavalent chromium compound, such as chromic acid mist in air, with organic dyes. For this purpose we have found that Methyl Violet 2B and Basic Fuchsin are satisfactory. The two dyes are mixed in equal portions and diluted serially to produce the desired matching shade. Filter papers larger than the area of the impregnated material that is exposed during a test

are dyed in these solutions and dried in air. A core, equal to the diameter of the stain produced in the test is then mounted in a white ring to simulate the actual stained samples, and the series of permanent color standards are then mounted between plates of glass or clear colorless plastic that does not cause fading of the standards. For field work a set of three stains corresponding to 1.5, 3.7 and 7.4 mgs. per 10 cubic meters of air is generally satisfactory. When not in use the standards should, of course, be protected from light and heat. In this range the color change is approximately linear with concentration. At the American Standards Association threshold safety concentration of 1 mg. of hexavalent chromium per 10 cubic meters, 10 strokes of the 600 cc. pump will match the low-est standard.

Actual practice of the method using filter paper impregnated with the reagent given by way of example and following the details stated has shown that the method yields results within 0.5 mg. per 10 cubic meters for concentrations below 3.3 mg. per 10 cubic meters, and that at higher concentrations the accuracy is plus or minus 10 per cent of a given concentration. The practical evaluation of the existence of a health hazard and of efficiency of ventilating equipment does not require any greater precision. Accuracy could be improved by the use of a wider range of permanent color standards, but this is unnecessary for most field work. A complete determination can be made within six minutes by an inexperienced operator.

The phthalic anhydride that is preferred as the solid acid may be converted at least in part to phthalic acid by water present in the solvent or picked up by the humectant. Accordingly, it will be understood that this is contemplated by the term phthalic anhydride as used in the claims.

Impregnated materials prepared in accordance with the invention may be used also for the determination and quantitative evaluation of soluble hexavalent chromium dusts, as contrasted with mists, in air or other gases. This is done by passing the gas through the impregnated material and then placing the latter with its retained dust in a small dish of water and comparing the resulting stain with color standards.

In the foregoing description of the making of color standards reference was made to the coring out of the standard from a paper larger than the area of the test paper that is exposed to the atmosphere under test. This is an important factor in preparing such standards. Thus, if a circle of the diameter of the stain produced with the test paper is stained directly with the dye, the outside edge of the circle will be more strongly colored than the center due to capillary action. By using a larger disc or piece of filter paper, however, there may be cored from it a uniformly stained disc for mounting in a white ring.

According to the provisions of the patent statutes, we have explained the principle of our invention and have described what we now consider to represent its best embodiment. However, we desire to have it understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

We claim:

1. Means for colorimetric determination of hexavalent chromium comprising absorbent pa-

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per impregnated with s-diphenylcarbazide and a solid stabilizer which is non-volatile and solid at ordinary temperatures and pressures of the group consisting of aromatic acids, their anhydrides, and alkali metal salts having an acid reaction when dissolved in water.

2. Means according to claim 1 said solid stabilizer being phthalic anhydride.

3. Means according to claim 1, the absorbent paper being impregnated also with a humectant.

4. Means for colorimetric determination of hexavalent chromium comprising absorbent paper impregnated with a mixture of about 94 per cent of phthalic anhydride and about 6 per cent of s-diphenylcarbazide, and also with a humectant.

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