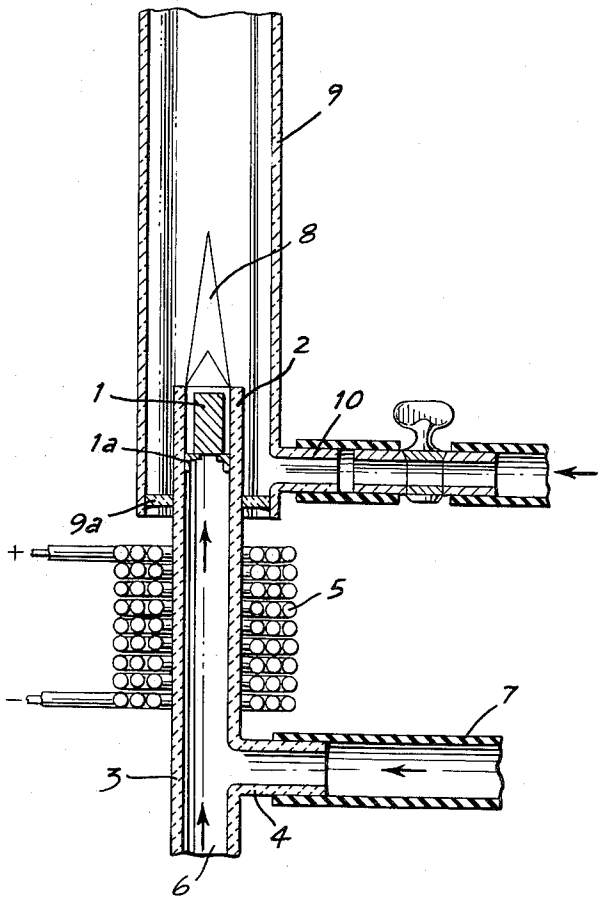
March 13, 1962 C. E. VAN DER SMISSEN 3,025,141

PROCESS AND APPARATUS FOR THE DETECTION OF HALOGEN-CONTAINING COMPOUNDS IN AIR

Filed Aug. 19, 1959 2 Sheets-Sheet 1

Fig. 1



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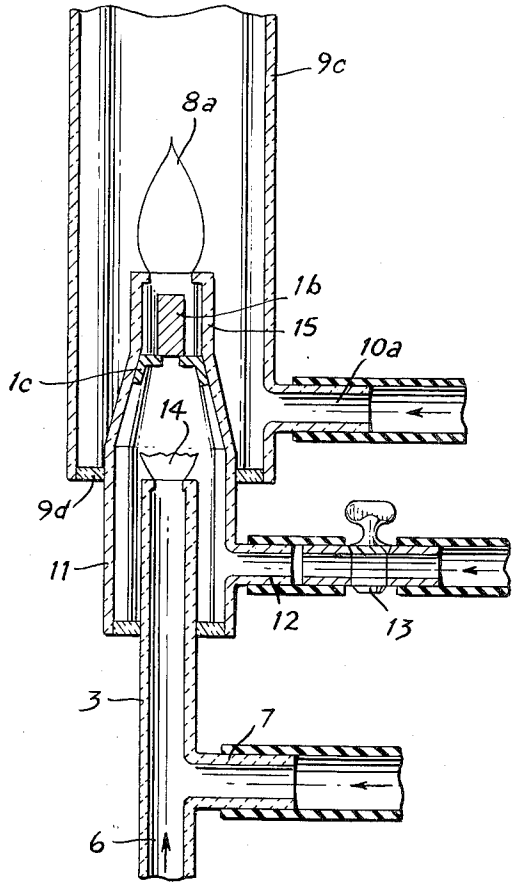


Fig. 2

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PROCESS AND APPARATUS FOR THE DETECTION OF HALOGEN-CONTAINING COMPOUNDS IN AIR

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This invention relates to the detection of halogen-containing compounds in air and, in particular, is directed to the detection of such compounds in air or other gases by a flame coloration in the presence of copper.

The Beilstein test for the continuous quantitative determination of volatile halogen compounds by the flame photometric method contains the difficulty in that the copper is placed in direct contact with the flame and is therefore easily destroyed by the heat of the flame. Furthermore, the shape of the flame is altered by the presence of the copper and thus produces a detrimental effect in the photometric results and, moreover, alters the surface of the copper sheet so as to make it unsatisfactory for use in further tests.

The object of this invention is to eliminate the disadvantages inherent in the conventional Beilstein test while testing the presence of halogens or halogen-containing compounds in air or other gases by flame coloration in the presence of copper.

In general, the invention comprises the mixing of the gas to be tested with a fuel gas, passing the mixed gases over heated copper, and then igniting the mixed gases to form a flame. Thus the copper is not placed in the flame and directly heated thereby, but is heated by a preheated fuel and gas mixture. A Beilstein flame is obtained which is highly suitable for photometric use. In the passing of the mixture of gases through a preheating zone, the gas to be tested is decomposed into halogen compounds which are carried into contact with the gas heated copper upon which copper halides are formed. These halides are then carried into the flame to produce the typical Beilstein color. If the copper is exposed to an oxidizing atmosphere, it is rapidly and progressively oxidized to its destruction. On the other hand, the maximum sensitivity of the Beilstein test cannot be reached if the copper sheet is exposed to a reducing atmosphere. The maximum sensitivity is obtained when a balance is established between the oxidation and the reduction of the copper in such a way that the copper is always coated with a thin oxide layer whose thickness does not vary substantially through the course of one test. For this reason, the temperatures of the copper and the gas mixture are so adjusted so that the copper is neither oxidized or reduced by the gas mixture.

The proportion of fuel gas and the gas to be tested is set so that the flame produced by the burner is not luminous.

For certain tests, the mixture of fuel gas and test gas is preheated prior to being brought into contact with the copper to a temperature at which the temperature to which the copper is heated is lower than that at which a catalytic combustion of the gas is initiated by the contact of the gas with the copper.

Such a test, for example, is when the components of the fuel gas and the test gas comprise an explosive gas. In this case, the copper may catalyze the fuel before the mixture of gases has reached the point of being ignited into the test flame, that is to say the photometric area. Above a temperature of approximately 300° C., the catalytic explosive gas combustion can be so active that the copper sheet is destroyed by the reaction heat. Consequently, in such a condition, the temperature of the copper must be kept below this catalytically limiting temperature. This catalytically limiting temperature is practically that at which the copper sheet is brought to a glow by the gas mixture flowing over it. At such a point, the mixed gases become catalyzed by the heated copper. Such a temperature can be prevented by applying additional cooling air to the outside of the burner pipe containing the copper. This additional air can be guided cylindrically around the flame. Consequently, the flow of additional air keeps the copper from being heated above a permissible temperature and, at the same time, can be used to stabilize the flame.

According to another feature of this invention, the flame can be divided into an inner lower flame and an outer upper flame at a predetermined distance above the lower flame so that the upper flame can be observed and recorded. The division of the flames is obtained by using two nested glass cylinders in order to obtain quiet constant flames, the upper of which is especially suitable for photometric purposes.

When the halogen component being tested for is the only flame coloring component of the gas mixture, the presence of the halogen is effected by a photometric measurement of the total intensity of the flame without subsequent amplification. The variations in the basic intensity of the flame are eliminated by a comparative measurement under the same conditions with a standard flame not containing the halogen component. This comparison is most effective when the flames are non-luminous.

The burner for the flame is preferably made of quartz or ceramic material.

The process of this invention has the advantage of being applicable to the continuous analysis of gas traces without complicated adjustments by reason of its high sensitivity and selectivity to halogen compounds.

The means by which the object of the invention is obtained are described with reference to the accompanying drawings in which:

FIGURE 1 is a cross-sectional view of the testing apparatus of this invention; and

FIGURE 2 is a similar view of a modification of FIGURE 1.

The copper member **1** in the form of a rolled sheet of copper or a wire netting is supported on a flange **1***a* in the upper end portion **2** of a burner **3**. For example, a thin sheet of copper approximately 20 x 60 mm. formed into a roll can be used. Burner **3** is composed of a T-shaped member in which the principal tube portion forms the head of the **T** and a test gas inlet **4** forms the leg of the **T**. The part of the burner **3** between the upper portion **2** and the inlet **4** is heated, for example, by being surrounded by an electrical heating resistance means **5**. Fuel gas is introduced into a lower end **6** of burner **3** and the test gas introduced through tube **7** joined to inlet **4**. The mixture of gases, after being heated by heater **5**, flows by and in contact with copper member **1** and is ignited to produce flame **8**. Surrounding upper portion **2** and the flame is a wide, transparent glass cylinder or chimney **9** which has its bottom end closed and spaced from burner **3** by the insulating asbestos ring **9***a*. Immediately above ring **9***a* is a branch pipe **10** which is connected to an additional fresh air supply.

In operation, burner **3** is heated by heater **5** to a temperature ranging between 600° and 900° C. Fuel gas is admitted through lower end **6**, test gas through pipe **7**, and additional air through branch **10**. The mixture of fuel and test gas being heated passes over copper member **1** and heats the copper to a temperature ranging be-

tween 300 and 450° C. Halogen compounds such as CCl_4, C_6H_5Br and CH_3I are decomposed and form with the copper copper halide which is carried along by the gas which is ignited to form the flame **8**. The presence of the halogen compounds causes a green flame. The intensity of the coloration is measured and recorded by suitable photometric means. The relation between the intensity of color and the halogen compound concentration is linear. The optimum measurement range is between 1 and 100 gamma (0.001 milligram) of halogen compound per liter of gas mixture. However, the range of measurement can be extended to a concentration of 10^{-7} to 10^{-2} grams of halogen compound per liter of gas mixture.

FIGURE 2 shows a modified apparatus in which the single flame of FIGURE 1 is divided and replaced by two flames. Burner **3** has its upper end portion **2** enclosed by a transparent glass chimney **11** having an air inlet pipe **12** containing a control valve **13**. As in FIGURE 1, fuel gas enters lower end **6** of tube **3**, and test gas enters through tube **7**. Flame **14** from the burning fuel gas and test gas mixture is regulated by the amount of air admitted into chimney **11** through pipe **12**. The narrowed upper end **15** of chimney **11** contains the rolled sheet of copper **1***b* resting on bracket **1***c*. Surrounding the upper half of chimney **11** is the outer transparent glass chimney **9***c* spaced from chimney **11** by the asbestos sealing ring **9***d*. Additional air is introduced into chimney **9***c* through pipe **10***a*. Test flame **8***a* burns at the upper end of chimney **11**.

The temperature of the copper **1***b* is kept between 400 and 700° C., preferably between 400 and 600° C., by regulating the quantity of air admitted into chimney **9***c* through pipe **10***a* in accordance with the heat produced by flame **14**. The mixture of fuel and test gases burns in lower flame **14** in the presence of air coming through pipe **12** with an incomplete combustion of the fuel gas due to the throttled air supply through valve **13**. The heated gases from flame **14** heat copper **16** and then the remaining fuel gases are finally consumed in test flame **8***a* in the presence of oxygen supplied through pipe **10***a*.

This modification has the advantage over the invention form of FIGURE 1, in that the copper can be heated beyond the catalytic spontaneous temperature point of the copper, that is, from 450° to 700° C. No catalytic reaction occurs as the oxygen supporting flame **14** is consumed before the gases reach copper **1***b*. Flame **8***a* is colored green if halogen compounds are present in the test gas, and the intensity of the color is measured and recorded by conventional colormetric means.

Before beginning a test, it is preferable to condition the surface of the copper member **1** by a short preliminary exposure of the copper to oxygen, then to hydrogen, and finally to the test gas containing the holgen compound, so that the maximum sensitivity is obtained immediately in the Beilstein test.

Having now described the means by which the objects of the invention are obtained, I claim:

1. A process for the colormetric detection of halogen compounds in a test gas ignited in a burner comprising mixing the test gas with a gas including a fuel gas, passing the mixed gases over and in contact with heated copper, and then immediately igniting the mixed gas to form a flame spaced from and without contact with said copper and colored in accordance with the presence of halogen compounds in the test gas.

2. A process as in claim 1 in which the composition of the mixed gases is such that the heated copper is neither oxidized nor reduced by said mixed gases.

3. A process as in claim 2, said mixed gases being proportioned to produce an initial non-luminous flame.

4. A process as in claim 3, said mixed gases being preheated before contacting said copper only to a point at which the temperature of the copper is less than that at which a spontaneous combustion is initiated by the contact of the mixed gases with the heated copper.

5. A process as in claim 4, further comprising cooling said heated copper wtih air applied to the burner.

6. A process as in claim 5, further comprising surrounding said flame with said air.

7. A process as in claim 6, further comprising forming an additional lower flame by partial combustion of the mixed gases beneath the upper color determination flame spaced from said lower flame.

8. A process as in claim 7, further comprising passing the heated exhaust gases from said lower flame over said copper.

9. A process as in claim 8, further comprising making a color comparison between a standard flame and the upper flame.

10. A process as in claim 1, further comprising heating said copper to a temperature ranging from 300 to 450° C.

11. A process as in claim 1, further comprising heating said copper to a temperature ranging from 400 to 700° C.

12. An apparatus for the colored flame determination of halogen compounds in a test gas comprising a nonmetallic burner tube, means for introducing a mixture of fuel gas and test gas into said tube, means for heating the gas mixture within said tube, and a copper insert in said tube spaced from the burner outlet end of the tube and in the path of the heated gases emitted from said tube so that said copper insert in not contacted by the flame formed at said outlet end.

13. An apparatus as in claim 12, further comprising a chimney over the burner end portion of said tube containing said copper insert, and means for admitting cooling air into said chimney and around said burner end portion.

14. An apparatus as in claim 12, said burner tube comprising an inner tube and an outer tube with said copper insert being in said outer tube, and said means for heating the gas mixture within the tube comprising means for admitting air into said outer tube for partially burning fuel gas at the upper end of said inner tube for heating said gas mixture.

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