THE SAMPLING OF HYDROGEN SULFIDE IN AIR WITH IMPREGNATED FILTER PAPER

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(Received November 5th, 1963)

In previous papers methods were described for the sampling of sulfur dioxide[1] and hydrogen fluoride[2] in air by drawing the air through impregnated filter paper. In these methods an aqueous solution of potassium hydroxide with added glycerol or triethanolamine was the impregnating fluid used. In the present paper it is shown that the same impregnated filters can be used for the collection of hydrogen sulfide in air if potassium zincate is added to the impregnating fluid to retain the hydrogen sulfide as zinc sulfide.

In the above-mentioned papers it was explained that the impregnated filter paper method will be most useful in sequential samplers fitted with impregnated tape and to replace impingers in field work. This is also true for the proposed method for hydrogen sulfide. It is comparable to the lead acetate paper method (see, *e.g.* JACOBS[3]), but the visual or photometric inspection of the formed fleck must be replaced by, for instance, the methylene blue method. This is more complicated but more precise and more sensitive.

EXPERIMENTAL

Filters

Filters (Whatman no. 1, diam. 5.5 cm) were prepared by impregnating them with 0.5 ml of fluid and heating at 100° until they were just dry. The impregnating fluid was prepared by dissolving 11 g of zinc oxide in 60 g of molten potassium hydroxide and dissolving this mixture—after cooling—in 360 ml of distilled water and 30 g of glycerol.

Some filters were exposed for a month to air with a relative humidity of about 50%.

Preparation of known concentrations of hydrogen sulfide in air of known temperature and humidity

The apparatus used is shown schematically in Fig. 1.

The necessary amount of air was supplied by a pump and valve. It was completely dried by silica gel and filtered. Known quantities of water were evaporated on a heated mica plate in the air-stream. The air-flow was measured, the excess air vented and the air-flow again measured. Then a known flow of hydrogen sulfide was added

and finally the temperature adjusted by passing the air through a few meters of teflon tube immersed in a waterbath. The humidity and hydrogen sulfide concentration were calculated from the air, water and hydrogen sulfide flows. The procedure was checked for temperature and humidity with a wet and dry bulb hygrometer. The hydrogen sulfide was generated in a Kipp apparatus. Its purity was determined iodometrically, or occasionally by potentiometric titration with silver nitrate.

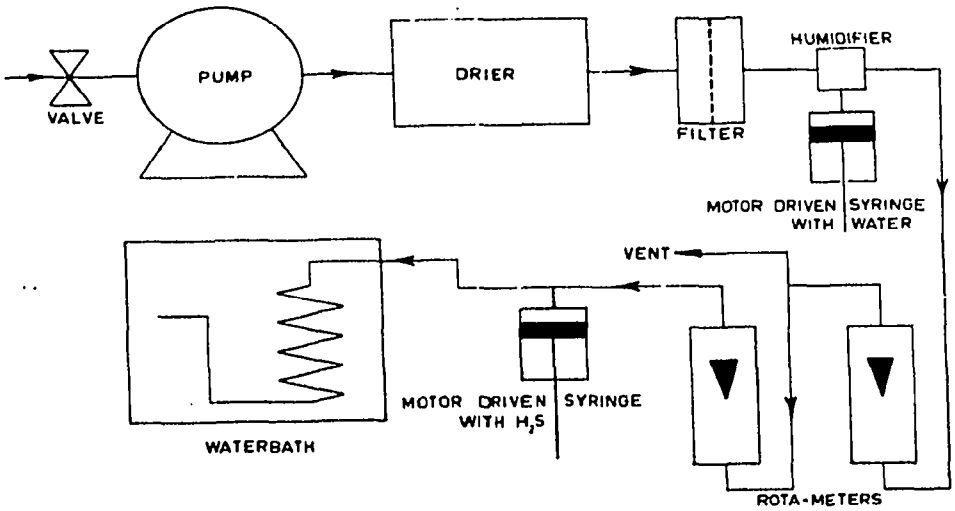

Fig. 1. Schematic of apparatus for preparation of known concentrations of hydrogen sulfide in air of known humidity.

Determination of the collection efficiency

As sketched in Fig. 2 the collection efficiency of a filter was determined by potentiometric titration[4] of the amount of hydrogen sulfide leaking through the filter.

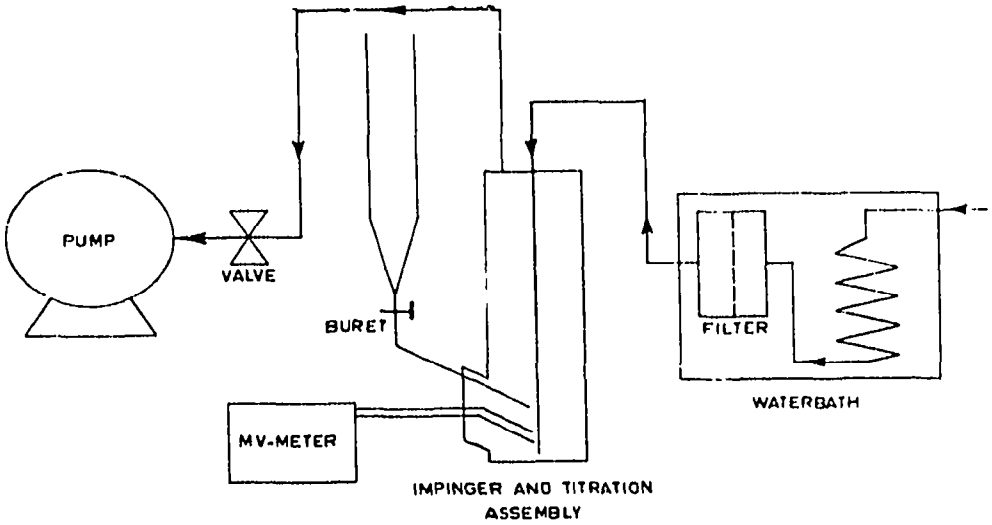

Fig. 2. Schematic of sampling apparatus.

The impregnated filter was clamped between plastic rings in a holder. The rings restricted the effective diameter to 4 cm. The filter holder was immersed in the water-bath used for the teflon tubing mentioned above.

After passing through the filter the air was bubbled through an impinger containing 0.1 *N* sodium hydroxide. Immersed in the solution were a silver/silver sulfide electrode and a sodium acetate salt bridge to a calomel electrode. The amount of 0.01 *N* silver nitrate necessary to keep the potential at the equivalence point was added from a buret. From this the amount of hydrogen sulfide leaking through the filter was calculated after correction for the collection efficiency of the impinger.

The required amount of air—generally 1 m^3/h—was drawn through the apparatus by a pump regulated by a valve.

Determination of the stability of the retained hydrogen sulfide

A known amount of hydrogen sulfide was sampled on impregnated filters as described above, the amount sampled being about 150 μg. One series of filters was then kept dry over silica gel, and another was kept at 70% humidity over a saturated salt solution, both at a temperature of 22°. After some time the filters were analysed for sulfide by the methylene blue method[5] as follows. The filter was put in a 100-ml Nessler glass and 80 ml of distilled water was added. The water was agitated by moving a glass stamper up and down in the glass, the neutralizing amount of acid was added and the solution was agitated again. Ten ml of reagent (0.44 g of *p*-amino-dimethylaniline per liter of 2.4 *N* sulfuric acid) were added and mixed. After a few min, 4 ml of 10% ferric chloride was added. The optical density was measured after 15 min at a wavelength of 670 mμ in a 1-cm cuvet.

All determinations were carried out in duplicate.

RESULTS

As a check on the hydrogen sulfide concentration the quantity found in the impinger was determined without any filter in the holder. It was, on average, 95.2% of the calculated quantity, which compares well with the collection efficiency of 95.7% determined by the two-impinger method.

Figure 3 gives an example of the graphical representation of the amount of hydrogen sulfide titrated in the impinger as a function of the time. As in the case of hydrogen fluoride there was a certain time of breakthrough; in the example given, this was 15 min. After this point the collection efficiency as calculated from the slope of the curve decreased; as shown in Fig. 2 the decrease was from 95% at 15 min to 80% after 30 min.

Times of breakthrough at various concentrations, humidities and temperatures are given in Figs. 4 and 5. The breakthrough time generally increased with decreasing concentration and increasing temperature and humidity as expected.

Another method of representation is shown in Figs. 6 and 7, where the total amount of hydrogen sulfide collected before breakthrough is chosen as the dependent variable.

Though there is some uncertainty because of the variability of the filters it is clear that the amount sampled generally increased with increasing temperature and humidity. The relation with the concentration is not so simple.

In the case of hydrogen fluoride it was found that the collection efficiencies depended not so much on the concentration and air velocity alone as on their product, which

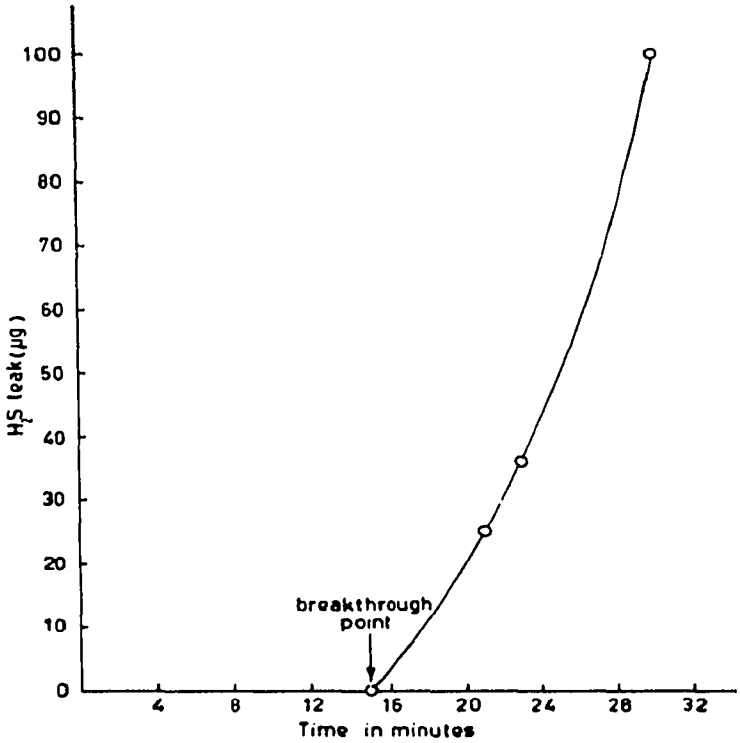

Fig. 3. Amount of H_2S leaked through the filter (concn., 4 mg/m³; humidity, 50%; temp., 20°; air-flow, 1 m³/h).

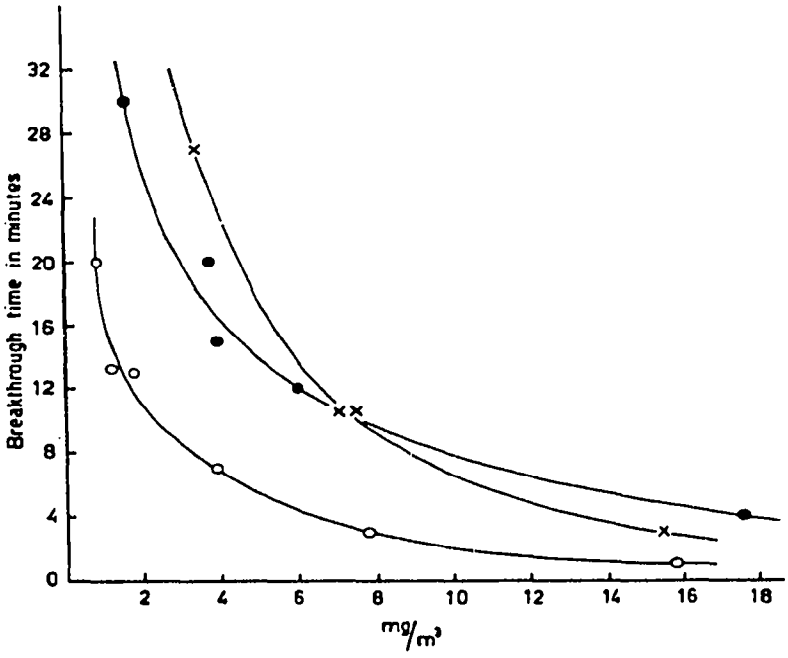

Fig. 4. Variation of time of breakthrough with increase of concn. at 20° (air-flow, 1 m³/h): ○, 25%; ●, 50%; ×, 90% humidity.

was called the rate of supply, *i.e.* the quantity arriving per unit of time at the filter. In Fig. 8 is shown the dependence of the time of breakthrough on the air velocity at constant rate of supply in the case of hydrogen sulfide.

In this case the breakthrough time and therefore the quantity sampled before

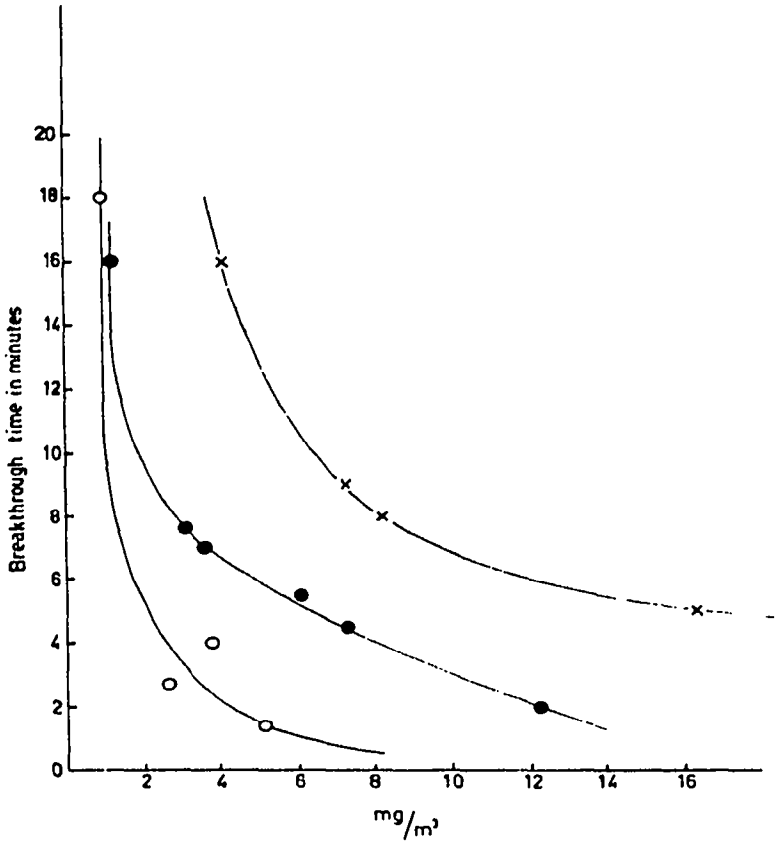

Fig. 5. Variation of time of breakthrough with increase of concn. at 0° (air-flow, 1 m³/h): ○, 25%; ●, 50%; ×, 90% humidity.

breakthrough depended strongly on the air velocity; they were in several cases almost inversely proportional to it. The curves shown in Fig. 8 were drawn as straight lines for lack of further experimental information, but they probably should have the form of hyperbolae, going asymptotic to both axes.

As found by titration to phenolphthalein and methyl orange indicators, the potassium hydroxide of the filters that were exposed to humid air for some time, changed to the extent of 60% into potassium bicarbonate and to the extent of 40% into potassium carbonate. The zinc was present as zinc carbonate. This will be the composition of the filters after a long sampling time. The collection efficiencies of the exposed filters were generally poor even at high humidities. The total quantity sampled before breakthrough was not more than a few tens of micrograms.

The stability of the sulfide collected on the filters may be gathered from Fig. 9.

There is hardly any loss in one month when the filters are kept dry. At 70% humidity the decrease is about 1.5% per day.

When the hydrogen sulfide was sampled on filters without zincate a loss of 85% in 2 h was found at 70% humidity.

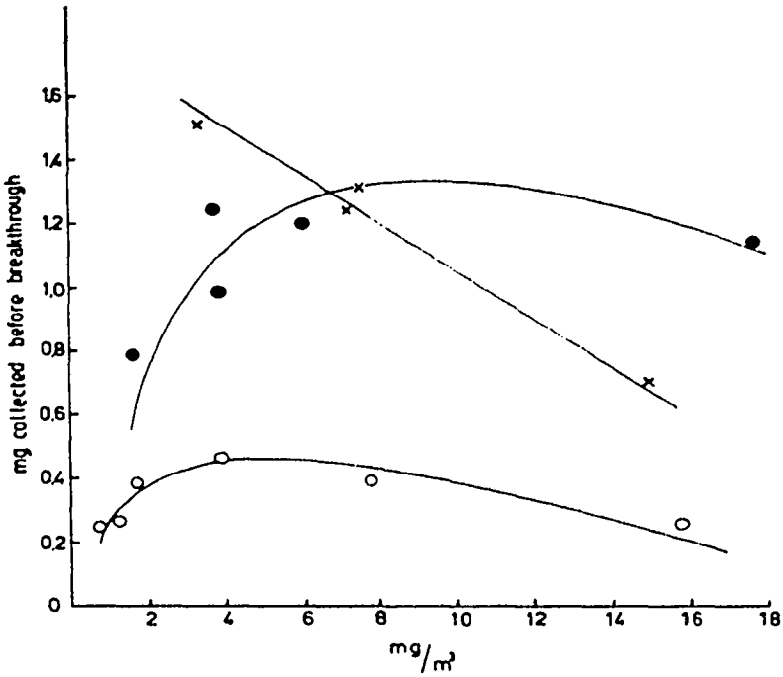

Fig. 6. Variation of quantity of H_2S collected before breakthrough, with increase of concn. at 20° (air-flow, 1 m³/h): ○, 25%; ●, 50%; ×, 90% humidity.

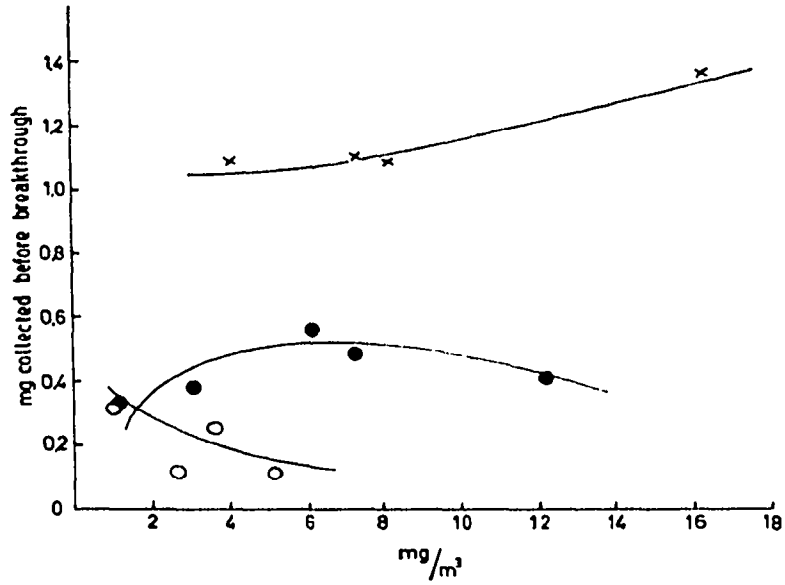

Fig. 7. Variation of quantity of H_2S collected before breakthrough, with increase of concn. at 0° (air-flow, 1 m³/h): ○, 25%; ●, 50%; ×, 90% humidity.

The quantity of hydrogen sulfide determined on the filters immediately after sampling was always a few per cent lower than the calculated value. Possibly the loss occurred during the determination, for a faint smell of hydrogen sulfide was detectable over the Nessler glasses, though the order of addition of the reagents and the form of the glasses were chosen so as to minimize losses.

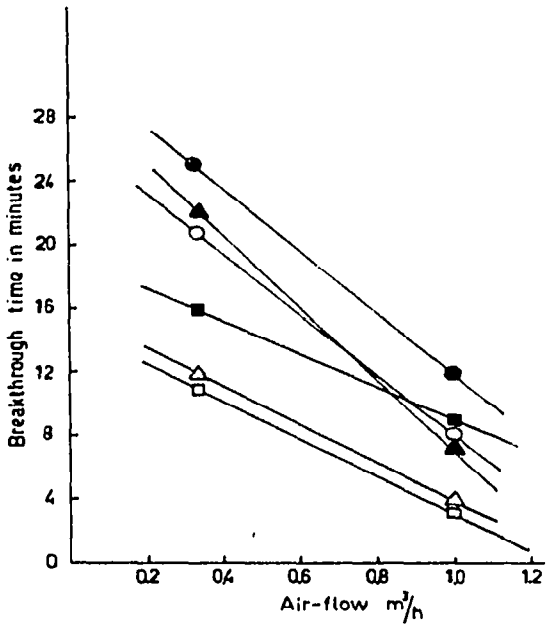

Fig. 8. Variation of time of breakthrough with increase in air velocity: ○, 20°, 25% humidity, 3.3 mg/h; ●, 20°, 50% humidity, 6.0 mg/h; ■, 20°, 90% humidity, 8.6 mg/h; △, 0°, 25% humidity, 3.7 mg/h; □, 0°, 50% humidity, 3.6 mg/h; ▲, 0°, 90% humidity, 7.3 mg/h.

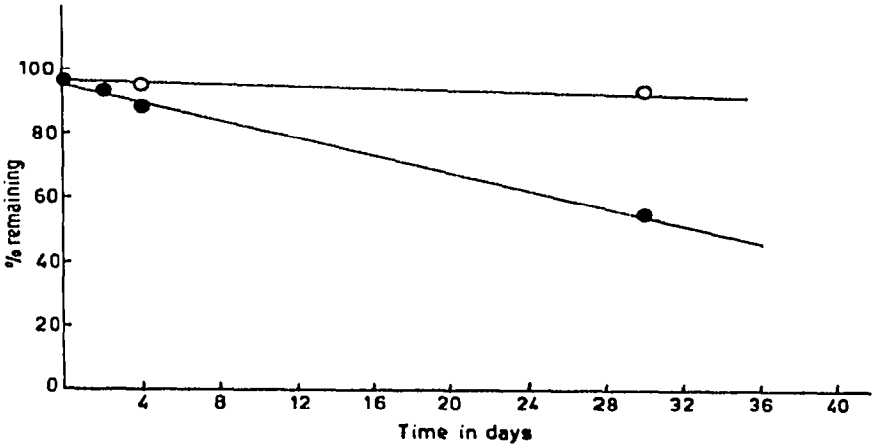

Fig. 9. Stability of collected H_2S: ○, kept dry; ●, kept at 70% humidity.

DISCUSSION

The picture of the mechanism of the collection of gases by impregnated filter paper as suggested by the results on sulfur dioxide[1] and hydrogen fluoride[2] is that the diffusion in the gas phase is comparatively fast, the rate of uptake being determined in the first place by the diffusion in the liquid phase. The gases are taken up at the surface of the liquid and the surface is "renewed" by the diffusion process.

With this picture in mind one expects the collection to be improved by increasing the humidity, because the collecting surface area is enlarged and the viscosity of the liquid decreased. An increase in temperature which furthers the diffusion, should also improve the collection. Lower concentrations would be expected to be better sampled because more time would be available for the regeneration of the surface of the liquid.

The results in the case of hydrogen sulfide are not completely in accordance with this scheme. It is less easily collected than sulfur dioxide and hydrogen fluoride, possibly because hydrogen sulfide is a weaker acid, escaping more readily from the surface of the liquid. The manner in which the amount collected before breakthrough depends on the concentration (Figs. 6 and 7) is not so easy to explain. The complicated behaviour may be caused by the addition of zincate to the impregnating fluid, insofar as precipitates are formed with hydrogen sulfide and carbon dioxide that may hinder the diffusion.

That the zincate addition is necessary and effective was proved by the experiments on the stability of sulfide on filters with and without zincate.

In practical air pollution measurements, the efficiency of the impregnated filters should be generally satisfactory, because the concentrations of hydrogen sulfide should not be higher than a few mg/m^3, whereas the humidity would be higher than 25%. Moreover, the efficiency does not drop immediately to zero after breakthrough (Fig. 3). Nevertheless the margin of safety is somewhat lower than in the cases of sulfur dioxide and hydrogen fluoride.

From Figs. 6, 7 and 8, can be derived the following general rules. Sample not more than 250 μg of hydrogen sulfide per filter at an air-flow of not more than 1 m^3/h; or taking into account the area of the filters: sample not more than 20 $\mu g/cm^2$ at an air velocity of not more than 22 cm/sec. Higher amounts can be sampled at lower air-flows. However, 250 μg is about the maximum amount which can be conveniently determined by the colorimetric method described, giving an absorbance of about 1.1.

Another important rule concerns the maximum sampling time. Because of the loss of efficiency resulting from the uptake of carbon dioxide and the limited stability of sampled sulfide, it is advisable to use a sampling time of certainly not more than 2 days. For the same reasons filters must be used fresh if possible, and should be stored in a dry, and if possible carbon dioxide-free atmosphere before and after sampling.

Up to now, more than 100,000 samples of hydrogen sulfide in air have been taken and analysed by our laboratory by the proposed method; in part the automatic sampling and analysis described in the paper on sulfur dioxide[1] was applied.

SUMMARY

A method is proposed for the quantitative collection of hydrogen sulfide in air on impregnated filter paper. An aqueous solution of potassium hydroxide, potassium zincate and glycerol is used as impregnating fluid. The stability of the collected sulfide and the efficiency of collection at different humidities, temperatures, hydrogen sulfide concentrations and air velocities were determined.

RÉSUMÉ

Une méthode est proposée pour la collection quantitative de l'hydrogène sulfuré dans l'air sur papier filtre imprégné. On utilise comme réactif d'imprégnation, une solution aqueuse d'hydroxyde de potassium, de zincate de potassium et de glycérol. L'influence de divers facteurs (humidité, température, etc.) a été examinée.

ZUSAMMENFASSUNG

Es wird eine Methode vorgeschlagen, mit der sich Schwefelwasserstoff aus der Luft quantitativ mit imprägniertem Filtrierpapier sammeln lässt. Als Imprägnierungsflüssigkeit wird eine wässrige Lösung von Kaliumhydroxid, Kaliumzinkat und Glycerin benutzt. Es wurde die Stabilität der gesammelten Sulfide und die Wirksamkeit der Sammlung bei verschiedenen Feuchtigkeiten, Temperaturen, Schwefelwasserstoffkonzentrationen und Luftgeschwindigkeiten bestimmt.

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