

A SIMPLE METHOD FOR THE DETECTION AND DETERMINATION OF HALOGENATED ORGANIC COMPOUNDS

Alvaro Alfonso
HOELZLE UND CHELTUS
Hugenottenallee 150
D 6078 Neu-Isenburg 1
F.R.G.

Abstract

Present work describes an experimental set-up to process samples of air, water and soil in order to detect pollution by halogenated organics. The basic principle is the optoelectronic evaluation of the intensity of the green flame produced when vapours containing the contaminants impinge on a heated copper spiral (Beilstein's test). Results obtained with simulated samples show that the method is sensitive and reproducible although it only gives the sum total of halogenated compounds and does not distinguish each component. Further work is in progress to miniaturise the set-up.

Introduction

The laboratory detection and determination of halogenated organic compounds using sophisticated methods like gas-chromatography, HPLC etc. present no problems. What seems to be of great use, is a field method which can supply rough information where exactly is the environmental contamination present so that relevant samples can be collected for further laboratory investigation. This consideration prompted us to investigate a simple and reliable method to process air, water and soil samples in, for example, accidental pollution cases where it is urgently required to pinpoint the place where a contamination with halogenated organics has taken place and if so whether the contamination is light or heavy and whether the contaminant is easily volatile or not. In the first instance, therefore, we had to devise an extremely simple and quick method to process air, water and soil samples in order to liberate the contaminant which had then to be detected and estimated at least semi-quantitatively. Our choice for a basic principle to sense halogenated organics fell on the well-known copper-wire test according to Beilstein¹. The test is however of a pure qualitative nature and meant for single determinations. We had therefore to optimize a set-up to generate the green flame of the Beilstein test continuously and then apply opto-electronic methods to correlate the green flame intensity with the concentration of the halogenated compound. It is interesting to note at this stage that we found that the oxidation of a large number of halogenated organics proceeds to 100 % completion when the same takes place with black copperoxide as catalyst in an atmosphere of butane or propane. The reaction products burn with a green flame and can therefore be detected. This fact provided us with a simple method to liberate the halogen directly from the sample which would be a safe procedure in case of dangerous substances like Dioxins and related substances. The instrumental set-up in its innovative form is described in our German Patent².

Experimental

Figure 1 shows the schematic diagram of a laboratory set-up consisting of a sample treatment part A, and the detecting part B of an instrument we constructed for field use. The legend to the figure in conjunction with the following text makes clear the working of the unit in case of air, water and soil surveillance.

1) Air surveillance: The taps 19 and 20 are closed. The air to be analysed is sucked by the miniature pump 17 and streams from tube 13 into a larger tube 12 at such a rate that the inlet air from tube 11 which is connected to the sensor unit B is absolutely representative. The micromanometer 14 serves as control. The sample is sucked at an uniform rate by the Venturi 4 of a Bunsen burner 5 and impinges then onto a copper spiral 6 which is further enveloped by flame 7 which is adjusted by valve 2. This arrangement ensures that the copper spiral is always within the oxidising part of the flame and hence produces the green flame when vapour containing halogens impinge on it.

2) Water surveillance. The water sample (2 liters) is extracted for just 4 minutes with 10 ml dodecane using a high speed Blender (about 8000 rpm.) working on 6 V. batteries. The extracting solvent is distributed as extremely fine droplets which coalesce within a few minutes to form a layer from which an aliquot can be easily pipetted. The sample is placed in container 15 which is equipped with controlled heating to 110° C. When air, filtered through charcoal, contained in container 16 bubbles through the heated dodecane the halogenated organic is stripped and leaves through tap 20. The high boiler dodecane produces hardly any interfering vapour. The detection step is the same as described above.

3) Soil surveillance. Soil samples (about 50 g) are extracted with dodecane 20 ml. The dodecane aliquot is processed and detected as above. Alternatively one can use the electrically heated container 15 to process directly a soil sample.

Results.

To establish the performance of the unit we calibrated the instrument first with air samples having definite concentrations of Trichloroethylene using the standard method of the "Kommission zur Prüfung gesundheitsschädlicher Arbeitsstoffe"³. A cross-check with gas chromatography was also performed. Test samples of air, water and wet clay soil were contaminated with trichloroethylene in such concentrations which corresponded to the limits and also to below limits prescribed in the MAK list and the "Trinkwasser Verordnung 1986" of the official organs of West Germany. Table 1 summarises the results

	Air sample	Water sample	Soil sample
Gas-Chrom. anal.	25 ppm	0.01 mg/l	31 mg/kg
	40 ppm	0.002 mg/l	20.6 mg/kg
Instrument descri	27 ppm	0.008 mg/l	33 mg/kg
bed	42 ppm	0.018 mg/l	22.3 mg/kg

Discussion

Results show that the set-up described is capable of yielding quick and reasonably accurate results with simulated contaminated samples. The limitations of the method is its inability to distinguish each contaminant; it only shows the sum total of all halogenated organics. However, due to its remarkable sensitivity it is possible to extend the use of the principle described. Further work is in progress to establish the use in actual field application to monitor the contamination caused by burning plastics and impregnated textiles. Favourable results have been obtained with preliminary adsorption on special silica followed by thermal desorption into very small volumes of air which are then made to impinge on the copper spiral.

References

1. Keller A. Nature 167 (1951) 907
2. Affonso A. Patent DE 3540509.0-52 of 14/5/1990
3. Luftanalysen Band 1 Verlag Chemie Weinheim 1976 Spezielle Vorbemerkung page 1

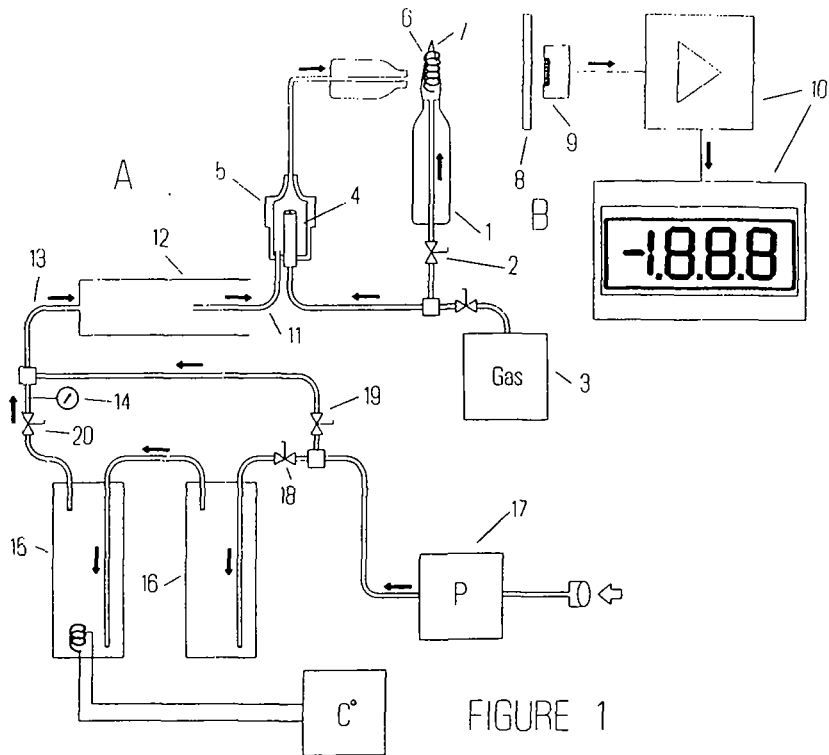


FIGURE 1

Legend to Figure 1

A sample treatment part B Detection part 1. Quartz capillary tube
 2. Gas regulation valve 3. Propane gas flask 4. and 5. Bunsen burner
 and venturi 6. Copper wire spiral 7. Microflame 8. Interference filter
 565 nM 9. Diode receiver 10 Amplifier for Digital Analogue display
 11. Aspirating tube for B part 12. Equilibration tube 13. Exit tube
 of A part 14 Micromanometer 15. Dodecane heating tube with heat
 regulator 16. Charcoal filter 17. Mini airpump 18. 19. 20. valves