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Note

High boiling organic traces in drinking water

Quantitative analysis by liquid–liquid enrichment within the analytical glass capillary

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The latest European regulations about drinking water analysis make it necessary to check for a wide variety of organic key compounds in drinking water in the sub-ppb[a] range. Without primary enrichment, more or less all regulated analytical methods available today are unsuitable for this purpose. There are in addition serious problems of taking, storing and manipulating the sample which may lead to incorrect determinations, and simple technical and human problems when the enrichment step commences with sample volumes of $\geqslant 1$ l water.

It is known that any surface adsorbs/desorbs any trace until an equilibrium is reacted between the phases and the matrix. This process is controlled by displacement chromatography at quite slow rates of material transport. Therefore large volumes of water in a completely full bottle may stay stable for weeks providing there are no biochemical changes or no mechanical movement by means of temperature gradients or mechanical forces. From such a large volume (litres) a small subsample (few ml) can be taken and placed into a freshly flamed glass container without further contact with surfaces, etc. The final container can be made absolutely clean outside as well as inside. We use flame stable coloured glass (ws in Fig. 1) heated in clean air to above 450°C and then cooled in clean air.

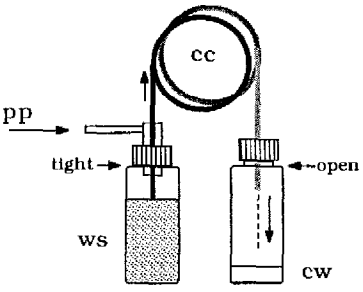

Fig. 1. Passage of sample through the glass capillary: pp = programmed gas pressure; ws = water sample; cw = clean water after passage through the glass capillary (cc).

[a] Throughout this article the American billion (10^9) is meant.

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Let us consider PNA analysis in water at the level of 20 ng/l = 0.02 ppb (w/w). By avoiding any further manipulation step, the possibility of getting true accurate quantitative PNA data is increased. We enrich the PNA onto an immobilized 0.25 μm thick film of PS-089 (94–96% dimethyl- / 4–6% diphenylsiloxane) terminated on the inner glass wall of a 0.3 mm I.D. glass capillary. Through such a 20-m analytical glass capillary (no fused-silica columns for many and obvious reasons) the water sample is forced by pressure programmed nitrogen. The enriching analytical glass capillary also serves as the analytical separation capillary.

An analytical process with enrichment into a "zero volume" of a specific solvent and quantitative specific analysis directly within this enrichment system will avoid many trace analysis problems like contamination from added solvents, other chemicals like sorption repellers, transfer of concentrates, changing containers, etc.

We modified a very similar concept developed by Zlatkis and Wang[1] as described below (see Figs. 1–4).

A 5-ml volume of a drinking water sample was transferred to the flame cleaned flask (ws). A 20 m × 0.3 mm I.D. glass capillary (cc) was then inserted into the room temperature sample so as to make a gas tight seal. Nitrogen gas pressure was applied, starting with 0.3 bar, then increased to 3 bar within 6 min. After 30 min the water sample had been forced through the glass capillary (cc) at room temperature and the excess of gas had pushed the water out of the capillary. The inside of the capillary (cc) is coated with an immobilized 0.25 μm thick film of PS-089 (see above). Many organic traces at the sub-ppb level remain sorbed under these conditions. A second experiment with the same water sample showed 100% transfer from water into the capillary film of all six key PNAs.

The inlet of the glass capillary was placed into the cold sample inlet of a gas chromatograph and the outlet of the glass capillary was placed into the detector. A very thin extra resistance capillary connects the glass capillary outlet with the detector inlet in a T-piece configuration. About 10 to 30 mm of the glass capillary inlet remained in a cool portion of the chromatograph sample inlet or just outside in the laboratory atmosphere.

A low carrier gas pressure was applied at the detector–capillary outlet T-piece connection. The gas chromatographic (GC) oven was heated at 30°C/min to 320°C. All traces volatile enough at 320°C were back flushed into the cold inlet zone.

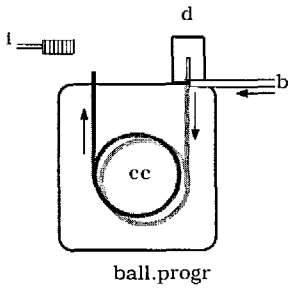

Fig. 2. Back flush and focusing of the wall-enriched sample traces: d = flame ionization detector; b = back flush gas, clean N_2; i = closure (septum) of the GC inlet, here open; ball.progr = temperature programme (30°C/min up to 320°C).

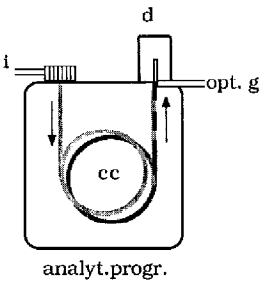

Fig. 3. Analysis of the enriched traces: opt.g = optimizing add-on gas for greater detector specificity and absolute quantitation, *i.e.*, to enable work at the response plateau; analyt.progr., for PNA analysis is shown in Fig. 4, initial temperature 50°C, then raised at 20°C/min to 160°C, followed by 7°C/min to 330°C.

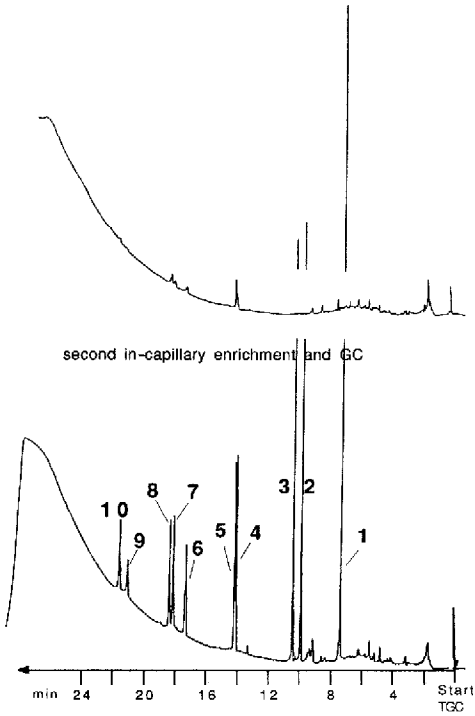

Fig. 4. Example of a chromatogram and of a check chromatogram of the "extracted" sample. Sample: 0.02 ppb each of anthracene (1), fluoranthene (2), pyrene (3), triphenylene (4), chrysene (5), benzo-[*k* + *b*]fluoranthene (6), benzo[*a*]pyrene (7), perylene (8), indopyrene (9), and benzo[*ghi*]perylene (10) in 5 ml water. Instrument: DANI 6500 gas chromatograph with flame ionization detection. Carrier gas pressures: inlet, p_i, 1.4 bar hydrogen; outlet, p_o, 0.5 bar nitrogen. In the upper chromatogram traces of PNAs 4–10 may be seen but no PNA 1 and 2! As no PNA traces are detectable in super clean "zero water" enrichments this may indicate a "memory" effect of the sample glass container prior to the "second extraction". We did not "flame clean" this container prior to the second experiment.

The GC oven was allowed to cool. The inlet was tightened, carrier gas applied and the inlet region heated. The enriched substances start to travel from a local position within the capillary as if they are being sampled on-line. However there is no diluting solvent! If sharp peaks are seen in the chromatogram there is no solvent effect nor retention gap effect, etc., *i.e.*, we have plain capillary GC of the substances. A 20-ng/l sample will contain 20 pg/ml = 5 × 20 = 0.1 ng total PNAs. There is no split nor any specific loss besides that which occurs during the storage of the sample in the 10-ml container (ws).

Temperature programmed GC of the in-capillary enriched substances extracted from the sample into the capillary phase film was then commenced.

The chromatogram was quantitated. We prefer the absolute quantitation using eqn. 1 but one can in addition work with artificial samples or add-on samples using many of the well known standard procedures for relative quantitation

$$\text{Concn. PNA}_x = it/q = hbE_1E_2A_S/q \cdot \text{FSD} \cdot P_SV_S \text{ (g/l)} \quad (1)$$

where i = peak signal in ampere, t = peak width at half height in s, or it = integral in coulomb, q = specific response in C/g for the PNA named x, h = peak height (mm), b = peak width (mm) or hb = integral of the PNA_x peak in mm^2, E_1, E_2 = sensitivity factors of the signal electronics, A_S = ion current in ampere producing a recorder signal of FSD (full scale deflection) in mm, P_S = paper speed (mm/s) and V_S = water sample volume in litre. The parameters h, b, E_1, E_2, A_S, FSD, P_S and q can be summarized as the integral value produced specifically by 1 g of PNA_x, *i.e.*, I_x.

REFERENCE

1 A. Zlatkis and F. Wang, *Anal. Chem.*, 55 (1983) 1848.