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Note

Variants of quantitative headspace analysis by multiple gas extraction of the sample

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Volatile compounds must often be determined in materials that cannot be charged into a gas chromatograph. This problem can be solved by employing the technique called headspace analysis. There are several variants of this technique, which differ in the instrumentation and operating procedures employed; however, the final step is almost always gas chromatographic (GC) analysis of the headspace gas.

The physicochemical basis of all the variants of headspace analysis is essentially the same. Namely, the volatiles in a condensed material are determined indirectly by GC analysis of the co-existing gaseous phase. In terms of this general definition, both dynamic (stripping) procedures and those in which gas-phase samples are withdrawn from static systems belong to the category of headspace analysis. The only difference between the above two alternatives is that the equilibration of the analyte between the condensed and gaseous phases proceeds continuously or discontinuously. In this work, the quantitative aspects of multiple-extraction headspace analysis are discussed.

PROCEDURES AND EQUATIONS

As early as 1966, Wahlroos and Nikkilä[1] published a theory of continuous-extraction headspace analysis. By meeting some assumptions, this theory can easily be extended to the discontinuous mode of the technique, *i.e.*, that of multiple-extraction headspace analysis. The latter variant was first described by Suzuki *et al.*[2] and McAuliffe[3] in 1970 and 1971, respectively. Since then this technique has been discussed by a number authors[4–12]. In our discussion, we shall concentrate on the quantitative aspects of headspace analysis by the multiple gas extraction of the sample, employing McAuliffe's[3] experimental arrangement as a model. The term "extraction" is used here only in a formal sense; it is simply the provision of a space for the analyte to pass from the condensed phase to the gaseous one, there being essentially no significant interactions between the molecules of the analyte and the "extracting" gas.

In McAuliffe's original variant, a volume, V_L, of the material to be analyzed and a volume, V_G, of a pure gas are successively drawn up into a syringe, the system is allowed to equilibrate and then the entire gas content is ejected from the syringe

by the piston into the sampling loop of a gas chromatograph and analyzed for the volatiles. This is considered as the first extraction step. Then another volume, V_G, of the pure gas is drawn up above the condensed material remining in the syringe, and the whole procedure is repeated n times. The initial mass of the analyte (i) in the condensed sample (and/or in the entire gas–condensed phase system) and the mass of the analyte in the gas phase of the system after the nth extraction will be denoted W_i and W_{iG}^n, respectively. We shall extend the concept to cover also the cases in which only an aliquot, v_G, of the gaseous phase in the system is withdrawn and analyzed by GC and those in which an entire gas–condensed phase system, rather than a condensed sample only, is the subject of analysis. A mention will be made also of the isochoric variant of this technique and of the continuous-extraction (stripping) technique.

Variant I

The subject of the analysis is a condensed sample of volume V_L. A volume, V_G, of pure gas is introduced, equilibrated, the volume V_G is ejected, followed by GC analysis, etc. (McAuliffe's original variant).

With this variant, W_i is related to W_{iG}^n by

$$W_i = W_{iG}^n \cdot \frac{KV_L + V_G}{V_G} \left(1 - \frac{V_G}{KV_L + V_G}\right)^{1-n} \tag{1}$$

where K is the condensed phase/gas partition coefficient of the analyte. This equation has been derived from the analyte mass balance and the Nernst distribution law. A logarithmic plot of eqn. 1 is shown in Fig. 1. It follows that

$$W_{iG}^{n=1} = W_i \cdot \frac{V_G}{KV_L + V_G} \tag{2}$$

and:

$$\frac{V_G}{KV_L + V_G} = 1 - \exp(d \ln W_{iG}^n/dn) \tag{3}$$

Hence, the quantity W_i can be expressed as:

$$W_i = \frac{W_{iG}^{n=1}}{1 - \exp(d \ln W_{iG}^n/dn)} \tag{4}$$

The quantity W_{iG}^n can be determined by any suitable conventional technique of quantitative GC analysis, *e.g.*, by the method of direct calibration, and $d \ln W_{iG}^n/dn$ is the slope of the straight line obtained by plotting $\ln W_{iG}^n$ against $n-1$. This slope can also be calculated from two successive determinations of W_{iG}^n, *e.g.*, from $W_{iG}^{n=1}$ and $W_{iG}^{n=2}$. Clearly, $d \ln W_{iG}^n/dn = \ln(W_{iG}^{n=2}/W_{iG}^{n=1})$, and eqn. 4 can be rewritten as:

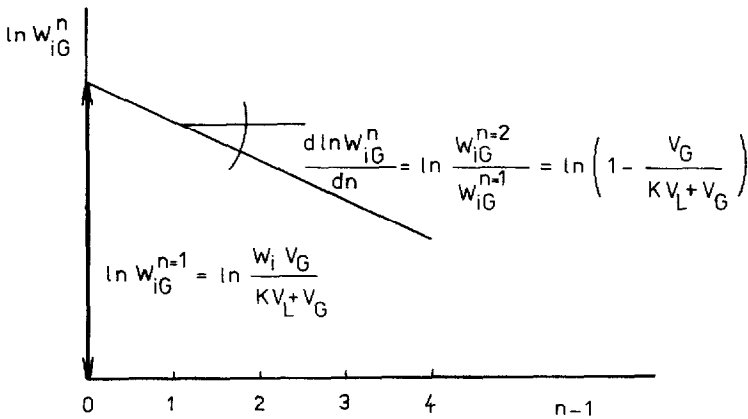$$W_i = \frac{W_{iG}^{n=1}}{1 - (W_{iG}^{n=2}/W_{iG}^{n=1})} \tag{5}$$

Fig. 1. Graphical representation of the situation in multiple gas extraction of the sample according to variant I (see the text). n is the serial number of the extraction steps, W_{iG}^n is the mass of the analyte in the gaseous phase of the system after the nth extraction step, $W_{iG}^{n=1}$ and $W_{iG}^{n=2}$ are the masses of the analyte in the gaseous phase of the system after the 1st and 2nd extraction steps, V_G and V_L are the volumes of the gaseous and condensed phases in the system, K is the analyte distribution constant, W_i is the initial mass of the analyte in the entire system (in the initial condensed sample), respectively.

The ratio $W_{iG}^{n=2}/W_{iG}^{n=1}$ is given by the ratio of the respective peak areas and/or peak heights in the chromatograms of the headspace gas samples. Eqn. 5 had been derived previously, but in a different way[4].

Variant II
    The subject of the analysis is a condensed sample of volume V_L. Procedure: introduction of pure gas of volume V_G, equilibration, ejection of volume v_G, GC analysis, introduction of pure gas of volume v_G, equilibration, ejection of volume v_G, etc.
    In this case eqn. 6 holds

$$W_i = W_{iG}^n \cdot \frac{KV_L + V_G}{V_G}\left(1 - \frac{v_G}{KV_L + V_G}\right)^{1-n} \tag{6}$$

and

$$W_i = W_{iG}^{n=1} \cdot \frac{v_G/V_G}{1 - \exp(d \ln W_{iG}^n/dn)} \tag{7}$$

and/or:

$$W_i = W_{iG}^{n=1} \cdot \frac{v_G/V_G}{1 - (W_{iG}^{n=2}/W_{iG}^{n=1})} \tag{8}$$

Variant III
    The subject of analysis is a system containing the condensed and gaseous

phases of volumes V_L and V_G. Procedure: ejection of the entire volume V_G, GC analysis, introduction of pure gas of volume V_G, equilibration, ejection of the entire volume V_G, etc.

The introduction of pure gas after ejection of the gaseous phase initially present in the system is considered as the first extraction step in this case, and

$$W_i = W_{iG}^n \cdot \frac{KV_L + V_G}{V_G} \left(1 - \frac{V_G}{KV_L + V_G}\right)^{-n} \tag{9}$$

and

$$W_i = \frac{W_{iG}^{n=0}}{1 - \exp(d \ln W_{iG}^n/dn)} \tag{10}$$

and/or:

$$W_i = \frac{W_{iG}^{n=0}}{1 - (W_{iG}^{n=1}/W_{iG}^{n=0})} \tag{11}$$

Variant IV

The subject of analysis is a system containing the condensed and gaseous phases of volumes V_L and V_G. Procedure: ejection of volume v_G, GC analysis, introduction of pure gas of volume v_G, equilibration, ejection of volume v_G, etc.

In this case we have

$$W_i = W_{iG}^n \cdot \frac{KV_L + V_G}{V_G} \left(1 - \frac{v_G}{KV_L + V_G}\right)^{-n} \tag{12}$$

and

$$W_i = W_{iG}^{n=0} \cdot \frac{v_G/V_G}{1 - \exp(d \ln W_{iG}^n/dn)} \tag{13}$$

and/or:

$$W_i = W_{iG}^{n=0} \cdot \frac{v_G/V_G}{1 - (W_{iG}^{n=1}/W_{iG}^{n=0})} \tag{14}$$

Isochoric mode of the technique

In isochoric modes of multiple-extraction headspace analysis[10,12] the gas-phase volume, V_G, above the condensed phase situated in a container is repeatedly pressurized from a pressure P to a pressure $P + \Delta P$ and de-pressurized to pressure P, the decompressed gas being analyzed by GC. In this case, $v_G = V_G \Delta P/P$, and we have, *e.g.*, for the isochoric analogue of variant IV,

$$W_i = W_{iG}^{n=1} \cdot \frac{\Delta P/P}{1 - \exp(d \ln W_{iG}^n/dn)} \tag{15}$$

and/or:

$$W_i = W_{iG}^{n=1} \cdot \frac{\Delta P/P}{1 - (W_{iG}^{n=2}/W_{iG}^{n=1})} \tag{16}$$

Note that the first de-pressurization (unlike the first ejection of a volume v_G in the isobaric mode) is considered as the first extraction step in this case.

Continuous-extraction (stripping) technique
        This technique can formally be looked upon as a limiting case of the discontinuous-extraction procedure with v_G approaching zero. Namely, if the extraction is carried out with a very large number of very small volumes of the gas, the process becomes quasi-continuous. In this case we can write, *e.g.*, for variant I:

$$W_i = W_{iG}^n \cdot \frac{KV_L + V_G}{V_G} \cdot \exp\left[\frac{(n-1)\,V_G}{KV_L + V_G}\right] \tag{17}$$

In stripping procedures, the total volume of the extracting gas that has passed through the system is given as Ft rather than $(n-1)V_G$, F and t being the volumetric flow-rate of the gas and the stripping time, respectively. Hence, eqn. 17 can be modified to

$$W_i = W_{iG}(t) \cdot \frac{KV_L + V_G}{V_G} \cdot \exp\left(\frac{Ft}{KV_L + V_G}\right) \tag{18}$$

where V_G is the volume of the gas space (plus gas bubbles) in the stripping vessel. It follows from eqn. 18 that:

$$W_i = -\frac{F}{V_G} \cdot \frac{W_{iG}(t=0)}{\mathrm{d}\ln W_{iG}(t)/\mathrm{d}t} \tag{19}$$

CONCLUSIONS

        All the experimental variants of multiple-extraction as well as continuous-extraction headspace analysis are based on one and the same principle, *i.e.*, the GC monitoring of the exponential decay of the analyte concentration in the gaseous phase of the system under specified conditions. The quantitative relationship between W_i and W_{iG}^n, once derived for a given variant of the technique, can easily be modified so as to make it applicable to another variant. However, it is necessary to consider carefully all the experimental variables in order to obtain a correct relationship between W_i and W_{iG}^n and/or $W_{iG}(t)$ for a given experimental variant of headspace analysis by the multiple and/or continuous extraction of the sample with a gas.
        In quantitative headspace analysis, the matrix effects ensuing from the distribution of the analyte between the phases of the system may be eliminated. However, it must be pointed out that the co-extraction of other components of the system may

cause gradual changes in the partition coefficient of the analyte during the course of extractions, which would apparently lead to inaccurate results.

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