zu entkräften. Dabei wurden die in Frage kommenden Störstoffe direkt mit DIP titriert, was in der Literatur bisher noch nicht beschrieben wurde. Da Redukton bei raschem Arbeiten nicht miterfasst wird[8] und es ausserdem im Handel schwer zugänglich ist, wurde darauf verzichtet, es in die Untersuchungen aufzunehmen. Die oben genannten Substanzen wurden in reiner Form (gelöst in HPO_3) bzw. als Zusatz zum Pflanzenextrakt (PE) gegen DIP titriert.

Unsere Ergebnisse bestätigen noch einmal eindeutig die Spezifität der Methode (Tabelle). Es muss allerdings wiederholt werden, dass diese Untersuchungen nur an Proben aus frischem Pflanzenmaterial durchgeführt worden sind und die Methode auch nur dafür gilt. Für andere Fälle, zum Beispiel Bestimmung von AS im Pflanzenmaterial aus Konserven oder in gekochten Proben usw., in denen weitere reduzierende Stoffe in grösseren Mengen auftreten können, müsste die Spezifität gesondert geprüft werden[9,10].

Summary. The following substances, which occur naturally in plants, do not interfere with the titration of ascorbic acid with 2,6-dichlorophenolindophenol (DIP): reduced glutathione, cystein, pyrogallole, brenzcatechin, hydrochinone, tannin, glucose and fructose. This is also true for the titration with DIP of high unphysiological concentrations of these substances dissolved in HPO_3 solution.

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Landwirtschaftliche Versuchsstation der BASF, 6703 Limburgerhof (Deutschland), 22. Juni 1966.

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[9] Herrn Professor Dr. Ed. Hofmann und Herrn Professor Dr. A. Amberger danke ich für ihre Unterstützung sowie die zahlreichen wertvollen Anregungen und Ratschläge.

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A New Method for Assay of Radioactive Dimethyl Sulfoxide and its Metabolite, Dimethyl Sulfone

Cotton and Francis[1] made an extensive study of metal complexes of dimethyl sulfoxide (DMSO). With $SnCl_4$ a white insoluble complex is formed having the composition[2] DMSO · $SnCl_4$. However, Lindqvist[2] observed no complex formation between $SnCl_4$ and dimethyl sulfone ($DMSO_2$), and we have confirmed this observation. Since $DMSO_2$ is a metabolite of DMSO in man and animals[3-5], it occurred to us that this difference in behavior of DMSO and $DMSO_2$ toward $SnCl_4$ might be useful as a means of estimating each substance in mixtures of the two. Although radioactive DMSO and $DMSO_2$ may be separated and estimated by paper or thin-layer chromatography[4,6], the method described here seemed to possess an inherent advantage in its simplicity. Separation and estimation of the compounds by gas chromatography (Hucker, Miller, and Hochberg[7]) is less simple but essential for analysis of non-radioactive samples.

The procedure used was as follows. Aliquots of standard solutions of DMSO and $DMSO_2$ in chloroform were diluted to 7 ml with chloroform in 15-ml glass-stoppered centrifuge tubes. Radioactivity in a 0.2 ml aliquot was measured by liquid scintillation spectrometry. 0.1 ml of non-radioactive DMSO was added, the contents mixed well, followed by addition of 0.1 ml of $SnCl_4$. After thorough mixing, the tube was centrifuged, and the radioactivity in 0.2 ml was measured. The results are shown in Table I. Recovery of DMSO was represented by the difference in c/min before and after precipitation. $DMSO_2$ remains virtually unaffected by $SnCl_4$ and hence the c/min before and after precipitation were nearly the same.

The DMSO and $DMSO_2$ content of mixtures was similarly calculated. Results of these analyses are shown in Table II. If mixtures of radioactive DMSO and $DMSO_2$ having a DMSO content that is appreciably higher than that of $DMSO_2$ are used, as was the case here, the counts after precipitation must be corrected for the small % of DMSO remaining in solution.

Table I. Precision and accuracy of determination of DMSO and $DMSO_2$

DMSO added, μg	DMSO found[a], μg	$DMSO_2$ added, μg	$DMSO_2$ remaining[a], μg
100	97.9 ± 2.1	50	44.6 ± 1.7
75	72.7 ± 0.5	25	22.6 ± 1.3
50	48.9 ± 0.3	10	9.0 ± 0.8
25	24.6 ± 0.2	5	4.3 ± 0.5

[a] Average of 5 determinations $\pm$ standard deviation.

Table II. Precision and accuracy of determination of DMSO and $DMSO_2$ in mixtures

Added DMSO, μg	$DMSO_2$ μg	Found DMSO, μg[a]	$DMSO_2$, μg[a]
100	25	103.0 ± 1.5	25.3 ± 1.9
50	10	49.7 ± 1.7	9.9 ± 0.8
25	5	25.8 ± 0.7	5.2 ± 0.3

[a] Average of 5 determinations $\pm$ standard deviation.

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Urine of 3 rats given DMSO-S^{35} (0.5 ml/kg i.p.) was collected for 24 h and assayed for DMSO and $DMSO_2$ by this method with the following results (expressed as a ratio of $DMSO_2$ to DMSO content): rat 1, 0.23; rat 2, 0.30; rat 3, 0.25. Quantitative gas chromatographic assay (HUCKER and MILLER[8]) gave the following ratios: rat 1, 0.25; rat 2, 0.35; rat 3, 0.24.

The present method appears to be a quick, accurate way to estimate DMSO and $DMSO_2$ content of solutions containing these compounds. It seems possible that the technique may also be applicable to the analysis of radioactive DMSO in mixtures containing other labeled compounds, provided the latter are not precipitated by $SnCl_4$.

Zusammenfassung. Es wird eine rasch arbeitende Methode für die quantitative Bestimmung von radioaktivem Dimethylsulfoxid und seinem Metaboliten Dimethylsulfon in Lösung beschrieben. Diese Methode beruht auf der selektiven Ausfällung von DMSO als Komplexverbindung mit Stannichloriden.

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Merck Institute for Therapeutic Research, West Point (Pennsylvania, USA), July 18, 1966.

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THEORIA

Theoretical Interpretation of the Saturation Effect in Irradiated Substances

The object of this investigation is the theoretical calculation of the dose-saturation effect by irradiation of a compound. In general, saturation effect means that the number of damaged molecules of a certain compound caused by irradiation (X-rays, γ-rays or fast electrons) does not increase steadily until all molecules are damaged, but reaches a constant value which will not be overstepped by further irradiation. This fact depends on the recombination of the radicals.

The mathematical description of this effect is based on the following model: During the irradiation the radical concentration increases and therefore the average distance between 2 neighbouring radicals becomes shorter. If the distance between 2 neighbouring radicals is small enough, these 2 radicals can recombine. This recombination depends also on temperature, so that recombination increases with mounting temperature.

The mathematical formulation is as follows: Let n be the number of molecules the sample contains. Then after irradiation, with the sample during the time t a constant dose rate, there are n_R radicals and $n - n_R$ undamaged molecules. Now we define

p_G: the expectation for generating radicals, and

p_V: the expectation for vanishing radicals.

The probability W_G for generating a radical with the next incident $h\nu$ is:

$$W_G = \frac{n - n_R}{n} p_G . \tag{1}$$

The probability W_V for a vanishing (recombination) radical is:

$$W_V = \frac{n_R}{n} p_V . \tag{2}$$

The increase dn_R of the radicals per time dt is given by

$$\frac{dn_R}{dt} = A\,(W_G - W_V) = A\left(\frac{n - n_R}{n} p_G - \frac{n_R}{n} p_V\right) \tag{3}$$

under the condition of constant dose rate. This differential equation (3) has the solution:

$$n_R = n \frac{p_G}{p_G + p_V}\left(1 - e^{-(p_G + p_V)\frac{A}{n} t}\right) \tag{4}$$

with the initial condition $t = 0$, $n_R = 0$. Here A is a proportional factor including the dose rate. The equilibrium between the generating and vanishing of radicals is reached if $W_G = W_V$. This yields:

$$n_{R\,max} = n \frac{p_G}{p_V + p_G} .$$

Eq. (4) is in accordance with the empirically found function of CONGER and RANDOLPH[1] for the dose-dependent radical yields in X-irradiated germ:

$$n_R = n_0\,(1 - e^{-\alpha D}).$$

Also many other investigators have observed an exponential dose-effect curve in irradiated substances. The recent literature is summarized in [2].

Zusammenfassung. Der bei der Bestrahlung mit ionisierenden Strahlen auftretende Sättigungseffekt, d.h. die Abweichung von der Linearität des Verhältnisses zwischen der Strahlendosis und der Zahl der geschädigten Molekeln bei höheren Dosisleistungen, wird unter Zugrundelegung eines einfachen Modells, welches sowohl die Erzeugung als auch die Rekombination der Strahlenschäden berücksichtigt, mathematisch beschrieben.

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CORRIGENDUM

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