

CCA-521

538.21

Original Scientific Paper

The Determination of Paramagnetic Susceptibilities by High-resolution Nuclear Magnetic Resonance

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Received July 3, 1968

Existing high-resolution NMR techniques for the determination of the magnetic susceptibilities of paramagnetic materials in solution are reviewed critically and the underlying theory is discussed. Attempts to measure the effect of interaction between indicator protons and paramagnetic ions suggest that, in the cases examined, this is less important than the change in field or frequency consequent on the insertion of paramagnetic material in the probe of a field/frequency locked spectrometer. Several variants of the substitution method have been tested. Provided that the calibration factor appropriate to the combination of tube and probe has been determined, a simple substitution method is practicable but, on the whole, the internal/external reference method with spinning concentric cylindrical samples is to be preferred.

INTRODUCTION

Since the review by Mulay,^{1,2} several variants have been proposed in the methods of determining magnetic susceptibility (χ) by nuclear magnetic resonance (NMR) spectroscopy. While Feher and Knight described a low-resolution NMR technique, in which crossed capillaries containing a reference liquid are embedded in powdered magnetic material³, it has been more usual to utilize high-resolution NMR chemical shifts in solution.

In the next part of this paper, the theory underlying the measurement of paramagnetic susceptibility by NMR is outlined. This is followed by a critical review of the experimental methods so far employed. Our own measurements are then described, and the results and their implications are discussed in the concluding paragraph.

THEORY OF MEASUREMENT OF PARAMAGNETIC SUSCEPTIBILITY BY HIGH-RESOLUTION NMR

Dickinson⁴ suggested that the average magnetic field, H_{av} , experienced by a given nucleus at resonance in a liquid be regarded as made up of four components:

$$H_{av} = H_0 + H' + H_d + H'' \quad (1)$$

Here, H_0 is the laboratory field;

H' is the shielding field at the nucleus as a result of the induced motions of the electrons in the isolated atom or molecule in question;

H_d is the bulk diamagnetic field; and

H'' is the field due to any paramagnetic ions present.

If the sum of the first three terms is unchanged when paramagnetic ions are added to a diamagnetic solvent, the corresponding change in proton chemical shift will depend only on the fourth term, H'' :

$$H_{\text{av, solution}} - H_{\text{av, solvent}} = H'' \quad (2)$$

If the chemical shift of a diamagnetic solute, such as 2% tert-butanol or dioxane (methylene protons), which does not interact with the paramagnetic ions, is used as marker, H' for the marker should be independent of the presence of the ions. Similarly, H_q , though not negligible, should remain unchanged when a small concentration of paramagnetic ions is introduced into the same container.

Following the electric dipole analogy, Dickinson⁴ then wrote

$$H'' = H_L + H_g + H_q \quad (3)$$

Here, the Lorentz or cavity field, H_L , is ascribed to the induced magnetic dipoles on the surface of a macroscopically small imaginary sphere, centred at the nucleus and just large enough to ensure that thermal motions of ions outside the sphere produce negligible field variations at the nucleus; H_L is given by $(4\pi/3)M$, where M is the volume magnetization of the sample consequent on addition of paramagnetic ions; $H_g = -dM$ is the demagnetising field; the demagnetising factor, d , depends on sample geometry: $4\pi/3$ for a sphere, 2π for an infinite cylinder. (From our experiments, 4 cm already gives a good approximation to infinity, in agreement with the conclusion of Zimmerman and Foster.⁵)

In theory, any interaction of the nuclear moments with fields from paramagnetic ions within the imaginary sphere should average to zero. Since he found this not to be the case, Dickinson⁴ introduced the third term in equation (3), $H_q = qM$, where the interaction factor, q , may be positive or negative. Thus

$$H'' = [(4\pi/3) - d]M + qM \quad (4)$$

For a cylindrical sample of infinite length,

$$H'' = (-2\pi/3)M + qM \quad (5)$$

If departures from a simple Debye-type theory are ignored and qM is neglected, we have the relation

$$H'' = (-2\pi/3)M \quad (6)$$

Neglect of qM enables one to predict correctly that H'' is negative, i. e. that the signal is shifted to higher fields.

NMR TECHNIQUES AVAILABLE FOR SUSCEPTIBILITY MEASUREMENT

High-resolution NMR techniques for susceptibility determination may be classified according to whether the solutions are contained in

(A) concentric cylinders, with (A/II) or without (A/I) spinning; or (B) a cylinder and an associated sphere.

(A) *Concentric cylinder methods*

(A/I) *Stationary sample*

Following a suggestion by Reilly *et al.*⁶, Fratiello^{7,8} and Li^{9,10} measured the volume susceptibility of an unknown sample contained in the inner of a pair of

stationary co-axial cylindrical tubes inserted in the spectrometer probe. Because of the non-uniform magnetic field which it experiences in the absence of spinning, the reference compound (generally benzene or cyclohexane) in the annulus has its resonance broadened to give a pair of maxima separated by $\Delta\nu$ Hz^{6,7,11} where

$$\frac{\Delta\nu}{4\pi\nu_0} = \chi_s \frac{a^2}{r^2} - \chi_g \frac{a^2 - b^2}{r^2} - \chi_r \frac{b^2}{r^2} \quad (7)$$

Here, χ_s , χ_g , and χ_r are, respectively, the susceptibilities of the sample, glass, and the reference compound; a and b are the inner and outer radii of the central tube; and r is the mean radius of the annular region. If reference and unknown sample are interchanged so that the sample is in the annulus, χ_s and χ_r in equation (7) must also be interchanged. Two methods, first, the insertion of reference standards in both inner and outer tubes, and, second, replacement of the inner central tube by a solid glass rod, yielded⁷ the same value, $-0.805 \pm 0.005 \times 10^{-6}$ c. g. s. u. for χ_g . Calibration of the cells¹⁰ and careful adjustment of X and Z magnet homogeneity settings¹² are generally necessary, but precisions from 0.5 to 2^{0/10,12,13} have been claimed. By observation of the effects of homogeneity adjustment controls, Douglas and Fratiello¹² were able to determine the sign of χ_s for dilute solutions of paramagnetic salts.

If measurements are confined to the same reference in the annular region of a standard set of tubes, equation (7) reduces¹³ to

$$\Delta\nu = A\chi_s - B - C \quad (8)$$

This linear relation may be used to calibrate the tubes directly with a series of compounds of known χ_s , thus avoiding the need to know a, b, r, χ_g and χ_r individually. The calibration line shifts vertically if the position of the tubes in the probe is altered, so that frequent re-calibration^{8,13} is necessary.

(A/II) Spinning sample

(A/II, 1) Internal/external reference method

According to Evans,^{14,15} the position of the NMR signal of an inert reference substance in an aqueous solution should depend, following equation (6), on the concentration of paramagnetic ions in the solution:

$$-\frac{\Delta H}{H} = K\Delta\chi_v \quad (9)^*$$

Here, $K = 2\pi/3$ and $\Delta\chi_v$ is the change in volume susceptibility. If the reference (2^{0/10} dioxane, acetone or, best, *t*-butanol) is, indeed, inert, it will presumably be legitimate to omit any allowance for interactions introduced by the q in Dickinson's rigorous treatment.⁴

Evans measured¹⁵ the frequency separation, Δf , between the resonances of equal concentrations of the marker contained in the paramagnetic solution and in a cylindrical capillary containing water; spinning of the main tube during the measurement also ensured that the capillary was concentric. If Wiedemann's law¹⁶ is assumed, the following relation obtains between Δf and the mass susceptibility, χ_{mass} , of the dissolved substance:

* The negative sign is consistent with the convention, which we use throughout, of positive shifts to weak field.

$$\chi_{\text{mass}} = - \frac{3 \Delta f}{2 \pi f m} + \chi_o + \chi_o \frac{(d_o - d_s)}{m} \quad (10)$$

(where f is the spectrometer frequency, m is the mass of substance in 1 ml of solution, χ_o is the susceptibility of the solvent, and d_o and d_s are densities of solvent and solution respectively). This was closely obeyed for several paramagnetic substances, particularly nickel chloride, for which accurate values of χ_{mass} , and its temperature dependence, are available.¹⁷

For diphenyldipicrylhydrazyl (DPPH), Evans determined¹⁵ χ_{mass} , as 2.46×10^{-6} c. g. s. u. by the same method, however, Friedrich¹⁸ was able to obtain exact agreement with the literature value (2.75×10^{-6} c. g. s. u.)¹⁹ for a chromatographically purified sample. Moreover, the same author found χ_{mass} in good agreement with the theory for several other free-radical species by the internal/external reference method.²⁰ In their extension of Evans' measurements to many paramagnetic compounds, including metal-organic π -complexes, Fritz and Schwarzahans²¹ neglected the last two terms in equation (10), and wrote

$$\chi_{\text{mass}} = \frac{\Delta f}{m} D \quad (11)$$

Instead of the expected value of $3/(2\pi \times 60 \times 10^6) = 0.796 \times 10^{-8}$, Fritz and Schwarzahans found by calibration with nickel chloride that the constant D was 1.06×10^{-8} , corresponding to $K = 1.57$.

In attempts to use equation (9) for determining the susceptibilities of diamagnetic substances, Bothner-By and Glick²²⁻²⁶ found that K varied within the range 2.33–3.00; deviation from the theoretical 2.09 was probably attributable to specific interactions in the binary systems studied.²⁶ Lussan carefully checked that K is 2.09 by dissolving small amounts of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ($< 0.1\text{M}$) in ethanol and measuring the shift (δ) of CH_2 relative to external water in a central co-axial tube.²⁷ Plots of δ against $\Delta\chi$ measured by a Pascal balance had gradient $2\pi/3$ within $\pm 10^{-8}$ when $\Delta\chi$ was smaller than 0.5×10^{-6} . Similarly, Friedrich²⁸ determined as 2.10 ± 0.05 the gradient of a plot of CH_3CN indicator shift against $\Delta\chi$ for solutions of DPPH in nitromethane; he found, further, that $K = 2.09 \pm 0.1$ for solutions of tetramethylsilane in 35 organic liquids, and $K = 2.07 \pm 0.1$ for DPPH in 10 solvents.²⁸

(A/II, 2) Separated-marker substitution method

An NMR spectrometer with an external field/frequency lock, such as the Varian A-60, may be used²⁹ in a rather different way for paramagnetic susceptibility measurements by determining the 'chemical shift' of water in the central of two co-axial tubes by successive measurements in the presence and absence of the material in question in the outer tube. The resonance frequency is a linear function of the magnetic induction at the nucleus, which itself depends on magnetic field intensity, and on the static volume magnetic susceptibility of the medium surrounding the nucleus. Calibration of the apparatus with a standard is necessary, and

$$\chi_{\text{unknown}} = \chi_{\text{standard}} \frac{\Delta H_{\text{unknown}}}{\Delta H_{\text{standard}}} \quad (12)$$

where ΔH is the appropriate 'chemical shift'.

(A/II, 3) Variation of field-axis method

In a spectrometer which has its magnetic field oriented parallel to the axis of the sample tube, as in the Varian HR — 220 superconducting solenoid spectrometer, the bulk susceptibility contribution of $(2\pi/3)$ in equation (6) is replaced by $(-4\pi/3)$. Recently, Dr. J. K. Beconsall (private communication) has suggested that this difference could form the basis of diamagnetic susceptibility determination through a chemical shift measurement relative to an external reference in a coaxial tube; this is placed in turn in a spectrometer with magnetic field parallel and perpendicular to the axis of the sample tube.

(B) Sphere and cylinder methods

In the Frei and Bernstein³⁰ NMR technique, a spherical sample tube and a cylindrical one touching it, both containing the same proton-rich reference liquid, are together immersed in a medium of different (unknown) susceptibility (χ_{sample}) in a conventional spinning sample tube. The separation, Δf , between the two reference signals is linearly dependent on χ_{sample} according to

$$\Delta f = \delta_{\text{cyl}} - \delta_{\text{sphere}} = E (\chi_{\text{ref}} - \chi_{\text{sample}}). \quad (13)$$

where δ_{cyl} and δ_{sphere} are, respectively, the chemical shifts of the reference in the cylinder and sphere, and E is a geometrical constant. (See also eq. 7 of ref. 42). In practice, E may differ slightly from the value of $2\pi/3 = 2.095$ appropriate to ideal cylindrical and spherical geometry so that it is best determined by a calibration graph of $\Delta\nu$ versus χ for compounds of known χ . Thus, Frei and Bernstein found $E = 2.058$ (15 compounds); Bartle,³¹ who applied the method to solvent fractions of coal tar,³² reported $E = 2.10$ (5 compounds); and Frost and Hall³³ found $E = 2.080$ (dioxane/water mixtures). If sharp lines are to be obtained^{30,34,35}, the magnetic field Y-gradient homogeneity control must be optimised carefully for each measurement. Frei and Bernstein claimed a surprisingly small mean deviation of 0.2% in³⁰ the susceptibilities of 15 compounds measured in this way, but a more realistic estimation of the precision of the method in routine use is probably the 2% standard deviation found for determinations on cyclohexane³¹. Mulay and Haverbusch modified the cylinder/sphere arrangement so that the cells were combined in one assembly³⁴; Y-gradient adjustments between one sample and the next were eliminated but calibration was still necessary. With bromoform as reference compound, they reported mean deviations of as low as 0.2% in susceptibility measurements on ferrohämoglobin.

EXPERIMENTAL

The need in studies of biological material³⁶ for a rapid simple method, with the minimum of specialised apparatus, spectrometer adjustment, and tedious calibration, led us to reject the methods A/I, involving stationary concentric cylinders^{37,38}, and method B involving a cylinder with associated sphere. Instead attention was concentrated first on the spinning concentric tube arrangements, A/II, and, second, on a technique that at the time was regarded as equivalent, namely the simple substitution method wherein chemical shifts of a marker are measured successively in water and in the unknown sample contained in the same or an identical tube.

General

All NMR measurements were made on a Varian A-60 spectrometer operating with a V-6058A spin-decoupler phase-lock in addition to the usual field/frequency

lock. Spectra recorded on the 100 Hz sweep width, were calibrated *versus* the separation between the resonances of a solution of 2% benzene, 2% TMS in CS₂, checked by an Advance J2 a. f. signal generator which was monitored by an Advance TC2 timer/counter. The probe temperature of 33° C was measured from the separation between methanol resonances. All results presented are the means of 5–10 runs and are estimated to be precise to ± 0.5 Hz.

Potassium ferricyanide solutions were made up by weight from A. R. material previously dried at 110° C; nickel chloride solutions (from A. R. nickel chloride) were analysed by precipitating nickel with dimethyl glyoxime. Cupric sulphate solutions were made up by weight from the A. R. pentahydrate.

*Internal/External reference method*¹⁵

Separations were measured between the methyl resonances of *t*-butanol (2%) in (a) nickel chloride, (b) potassium ferricyanide, and (c) cupric sulphate solutions in the outer of two spinning co-axial tubes (Wilmad Glass Co., Buena, N. J. 'coaxial cell units with precision spacing of inner tube' — Figure 1) and in distilled water

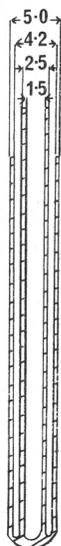


Fig. 1. Dimensions of coaxial cells in mm.

in the central tube. Measurements were made for two different cells. In another series of experiments, paramagnetic and reference solutions were interchanged. Spinning side bands seriously interfered with the identification of *t*-butanol lines in some of these determinations.

Simple substitution method

The positions of the 2% *t*-butanol signal in nickel chloride, potassium ferricyanide and cupric sulphate solutions, contained in standard Varian 5 mm O. D., 4.2 mm I. D., sample tubes were measured relative to the same reference signal in a distilled water solution; this was contained in another Varian tube substituted in the probe immediately after the first measurement. Signals from the same reference solution in different Varian tubes were reproducible to ± 0.2 Hz. For cupric sulphate solutions, the measurements were repeated with a tube of I. D. 3.6 mm.

*Separated marker substitution method*²⁹

A second substitution method was studied by measuring the resonance position of the 2% *t*-butanol marker in water in the inner of two concentric tubes (Figure 1), with the annulus first containing air and then nickel chloride solutions. After each solution measurement, the signal of the marker was recorded with distilled water in

this outer cell. If different cells were used, these latter measurements were no longer reproducible.

Measurements with spherical cells

An attempt was made to investigate the factor 'q' by determining the change in resonance position of 2% *t*-butanol in water containing different concentrations of nickel chloride in 4.5 mm diameter spherical microcells³⁹ (kindly supplied by Dr. G. E. Hall, Unilever Research Laboratory, Sharnbrook, Bedford). After each nickel chloride measurement, shifts relative to *t*-butanol in water were measured in the same cell. Care was taken to centre the height of each sphere accurately in the receiver coil; adjustments of homogeneity (particularly Y) and phase controls were necessary before satisfactory spectra could be recorded.

RESULTS AND DISCUSSION

Consistent changes in relaxation time, demonstrated by the large increase in line-breadth of the marker with concentration of Cu^{2+} and Ni^{2+} (Fig. 2.) (but

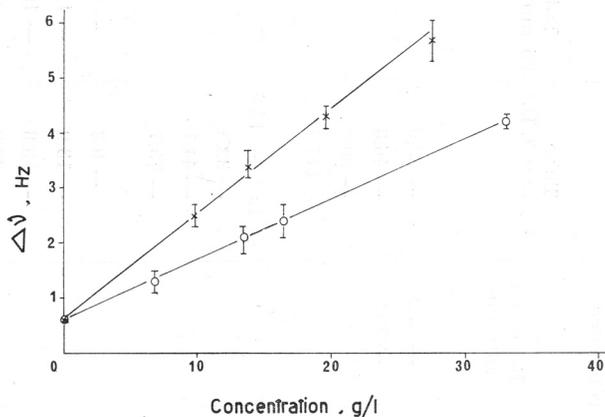


Fig. 2. Dependence of line-width of tertiary-butanol resonance on concentrations of CuSO_4 (x) and NiCl_2 (O) solutions; vertical lines represent range of observations for each experimental point.

not in ferricyanide solution), imply variations in magnetic and/or electric fields near the marker nuclei. As Evans noted,¹⁵ the effect is greater for Cu^{2+} with its effectively *s* state, than for⁴⁰ Ni^{2+} . Thus variation in the H_1 component of equation (3) might be expected to undermine the relevance of equation (6). However our determinations (Table I), taken with the results of Evans¹⁵ and of Friedrich,^{18,20} confirm that the internal/external reference method (A/II, 1) appears to give satisfactory values for χ_{mass} of paramagnetic materials.*

If the substance is placed in the central tube, there is the advantage that only small amounts of material are needed, but filling can present difficulties with viscous solutions. However, the requirement of a special cell, and the difficulties experienced with spinning side-bands, led us to investigate other simple substitution methods. Because of the high magnetic-field stability inherent in the locking systems of the A-60, the internal/external reference and substitution methods might be expected to be equivalent. In fact the measure-

* Nevertheless, we should like to emphasize that only for NiCl_2 did we find in the literature reliable values of magnetic susceptibilities, i. e. determined in solution and in dependence on temperature.

TABLE I
 Summary of Observed Indicator Shifts, Line-widths, and Corresponding Calculated Mass Susceptibilities for Varying Concentrations of Paramagnetic Solutions

Paramagnetic Material	Concentration gm/litre	Separation of <i>t</i> -butanol resonances (Hz at 60 MHz.)				Width at half-height (Hz) of <i>t</i> -butanol resonance in contact with paramagnetic solutions.	10 ⁶ mass-susceptibility, c. g. s. u. calculated from equation (10) [†] (Internal/external magnetic reference).
		Concentric tubes		Simple substitution			
		Internal / external reference	Reversed solutions	Tube 4.2 mm I. D.	Tube 3.6 mm I. D.		
		Cell 1	Cell 2				
NiCl ₂	6.7	-26.4	-26.8	-27.2	-23.0	1.3	31.8*
	13.4	-55.8	-53.4	-53.8	-46.8	2.1	32.3
	16.4		-66.5		-59.0	2.4	32.1
	32.9				-117.6	4.2	
K ₃ [Fe(CN) ₆]	20.7	-17.3			-15.2, -14.6		6.3**
	36.9	-36.2			-32.5		7.6
	49.3	-49.2			-44.1		7.6
	82.9				-75.7		
CuSO ₄	9.8	-10.9			-9.3	2.5	8.9***
	13.7	-14.6			-13.0	3.4	8.9
	19.6	-21.8			-18.8	4.3	8.9
	27.4	-30.5			-26.3	5.7	8.5

[†] Second and third terms total -0.1, -0.3, and 0 for NiCl₂, K₃[Fe(CN)₆] and CuSO₄ solutions respectively.

* Literature values: (33° C) 32.8 in H₂O solution¹⁷, (20 ± 1) 34.1 ± 0.3 in H₂O solution (this method)¹⁵.

** Literature values: (25° C) 8.11 in N HCl solution,⁴³ (15°) 6.43 in H₂O solution,¹⁴ (20 ± 1) 7.67 in H₂O solution (this method)¹⁵

*** Literature values: (20° C) 10.3 in H₂O solutions,⁴⁵ (20 ± 1) 9.6 in H₂O solution. (this method)¹⁵

ments summarised in Table I, and plotted in Figures 3 and 4, show that, in the simple substitution method, the shift to high field of the *t*-butanol resonance in the paramagnetic solution is always less than for the internal/external reference method.

It was first suspected that these discrepancies originated in the inclusion of the q factor, introduced by Dickinson,⁴ in the substitution determination, but

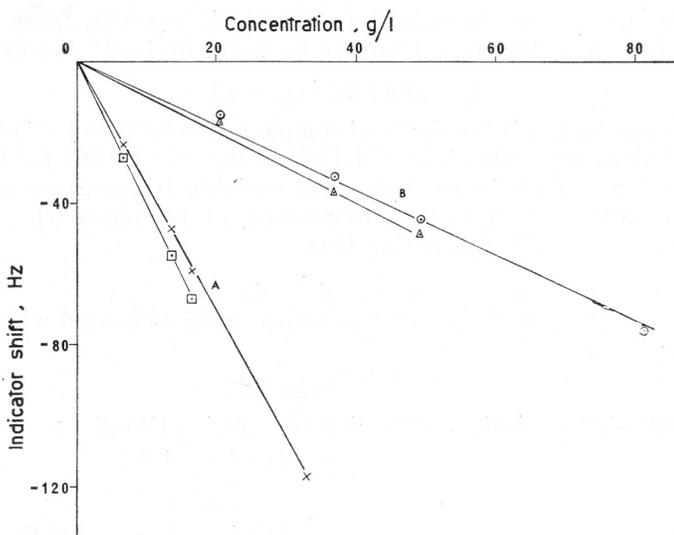


Fig. 3. Graph of indicator (*t*-butanol) shift against concentration of paramagnetic solution: (A) NiCl_2 , \square internal/external reference method; \times substitution method with tube 4.2 mm I. D.; (B) $\text{K}_3\text{Fe}(\text{CN})_6$, \triangle internal/external reference method; \circ substitution method with tube 4.2 mm I. D.

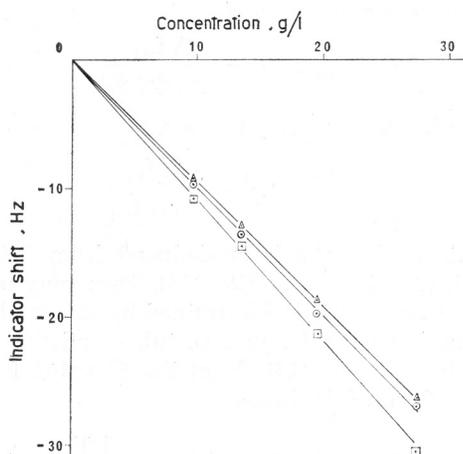


Fig. 4. Graph of indicator (*t*-butanol) shift against concentration of CuSO_4 solution: \square internal/external reference method; \circ substitution method with tube 3.6 mm I. D.; \triangle substitution method with tube 4.2 mm I. D.

not in the co-axial cell (external reference) method. A more plausible explanation⁴¹, is that the very introduction of a sample of different susceptibility into the magnet pole gap changes either (a) the magnetic field, by altering the reluctance of the magnetic circuit,⁴² or (b), for a field-frequency locked spectrometer such as the A-60, the frequency by changing the field in the region of the water-lock sample; the nuclear sideband oscillator then assures a corresponding change in the nominal 60 MHz frequency. Thus, for the internal/external reference method, the main-field environments of *t*-butanol in both sample and reference are similar; for the substitution method, however, there is an extra shift, δ' Hz, for which Baron and Lumbroso-Bader derived⁴¹ the expression

$$\delta' = G \pi h R^2 f (\chi_s - \chi_r), \quad (14)$$

where G is a constant, h is the depth of sample in the tube and R is the internal diameter of the sample tube; they determined the value 0.267 for $G \pi h R^2$ for 4 mm I. D. sample tubes in an A-60 with variable temperature probe, using acetone as sample (s) and hexamethylacetone as reference (r).

Writing $F = G \pi h R^2$, and noting that

$$\begin{aligned} \chi_s - \chi_r &= \chi_{\text{mass}} \frac{m - \gamma_o}{m} - \chi_o \frac{m - \gamma_o}{m} (d_o - d_s) \\ &= \chi_{\text{mass}} \frac{m - \gamma_o}{m}, \text{ if the last two terms, small compared with the first,} \end{aligned}$$

are neglected,

then

$$\delta' = \chi_{\text{mass}} m f F.$$

For the *substitution method*, modification of equation (10) gives

$$\begin{aligned} \chi_{\text{mass}} &= - \frac{3 (\Delta f_{\text{subst}} + \delta')}{2 \pi f m} \\ &= - \frac{3 (\Delta f_{\text{subst}} + \chi_{\text{mass}} f m F)}{2 \pi f m} \end{aligned}$$

$$\text{Rearranging, } \chi_{\text{mass}} = - \frac{\Delta f_{\text{subst}}}{(2 \pi/3 - F) f m} = - \frac{\Delta f_{\text{subst}}}{F' f m}$$

Now, for the *external reference method*

$$\chi_{\text{mass}} = - \frac{\Delta f_{\text{ref}}}{2 \pi/3 f m}$$

$$\text{whence } 2\pi/3/F' = \Delta f_{\text{ref}}/\Delta f_{\text{subst.}}$$

and

$$F' = 2 \pi/3 \frac{\Delta f_{\text{subst.}}}{\Delta f_{\text{ref}}} \quad (15)$$

Table II lists the values of F' we have deduced from NiCl_2 , $\text{K}_3[\text{Fe}(\text{CN})_6]$, and CuSO_4 solutions, with the aid of equation (15). They may be compared with the value of $F' = 2.095 - 0.267 = 1.828$, determined by Baron and Lumbroso-Bader⁴¹ in a similar apparatus but with 4 mm I. D. tubes and they help to confirm the R^2 dependence of δ' in equation (14): from the F' value for 4.2 mm I. D. tubes we calculate for the 3.6 mm I. D. tubes:

$$F' = 2.095 - (2.095 - 1.83) \times \frac{1.8^2}{2.1^2} = 1.90.$$

This is in agreement with experiment (Table II).

TABLE II

Experimental Values of the Constant F' , which Replaces $2\pi/3$ in the Equation for the Determination of χ_{mass} by the Simple Substitution Method

Compound	Concentration gm/litre	F'	
		Tube 4.2 mm I. D.	Tube 3.6 mm I. D.
NiCl ₂	6.7	1.80	
	13.4	1.81	
	16.4	1.86	
K ₃ [Fe(CN) ₆]	20.7	1.81	
	36.9	1.88	
	49.3	1.88	
CuSO ₄	9.8	1.79	1.88
	13.7	1.87	1.95
	19.6	1.81	1.90
	27.4	1.81	1.86
Mean		1.83	1.90

For the simple substitution method we therefore replace equation (10) by:

$$\chi_{\text{mass}} = \frac{-\Delta f}{F' f m} + \chi_o + \chi_o \frac{(d_o - d_s)}{m} \quad (16)$$

The measurements made with two spherical cells ($d = 4\pi/3$) by a substitution method (value of F' unknown) failed to realise an assessment of q *via* equation (11). Reproducibility was poor and although, as Table III shows, all the NiCl₂ shifts were to high field of the signal from *t*-butanol in water there was no overall correlation with concentration. Since each measurement involves removal of the cell, emptying and re-filling it, and relocation in the probe, errors arise, no doubt, from small variations in sample volume and in the exact position of the sphere in the coil.

TABLE III

Shifts in Hz of Indicator Peak between Solution and Solvent (Water) by two Substitution Procedures

Material	Conc. gm/litre	Separated indicator method	Spherical microcells	
			Cell 1	Cell 2
NiCl ₂	6.7	2.5	-1.6	-3.2
	13.4	4.2, 4.8	-2.3, -5.4	
	16.4			-2.5
	32.9	12.6	-2.0	-4.2
	65.8	23.3		
Air		7.9		

At first sight, the separated marker substitution method²⁹ appears promising for the determination of susceptibilities of biological materials; there should be no effects arising from contact of the marker with paramagnetic species. Although the separated marker shift, as determined by substitution method, depends linearly on NiCl_2 concentration (Table III and Figure 5), the very high

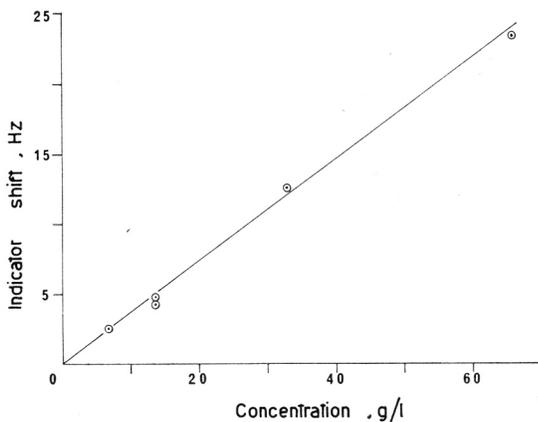


Fig. 5. Graph of indicator (*t*-butanol) shift by separated marker method against concentration of NiCl_2 solution.

concentrations required to produce significant shifts led us to abandon this method.

The spinning concentric tube technique remains the method of choice since prior calibration is unnecessary. However, provided that the value of F' appropriate to the probe and tube assembly has been established, the simple substitution method can be used with a field/frequency locked spectrometer for measuring small changes in susceptibility. On the other hand, shifts measured with the separated marker substitution method are too small to yield useful susceptibility measurements for solutions.

Acknowledgment. We thank I. C. I. Ltd., for a Fellowship awarded to K. D. B. and the European Molecular Biology Organisation for the award of a short-term fellowship to S. M., during the tenure of which this work was initiated and part of it carried out.

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IZVOD

Određivanje paramagnetskih susceptibilnosti metodom nuklearne magnetske rezonancije velikog razlučivanja

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Paramagnetske susceptibilnosti otopljenih tvari mogu se odrediti i mjerenjima razlike u pomaku protonske rezonancije nekog (inertnog) označivača kada je ovaj u čistom otapalu, te uz prisutnost otopljene paramagnetske soli. U ovom je radu dan kritički pregled nekoliko poznatih tehnika koje koriste uređaje velikog razlučivanja s tzv. spregom (magnetskog) polja i (rezonancijske) frekvencije. Potvrđen je rezultat da i u takvom eksperimentalnom uređaju dolazi do sistematske pogreške zbog promjene efektivne vrijednosti polja (tj. frekvencije) kada se u magnet unese uzorak s paramagnetskom otopinom. Nastojanja da se izmjeri promjena kemijskog pomaka zbog eventualne interakcije protona od označivača s elektronima paramagnetskog

iona pokazala su da je taj efekt (za ispitivane anorganske spojeve) zanemarljiv u poređenju s onim prethodnim. Svaki se uređaj može kalibrirati u odnosu na tu efektivnu promjenu polja (frekvencije) i onda zadovoljava metoda jednostavne supstitucije cjevčice u kojoj je otapalo s označivačem, drugom istovrsnom cjevčicom u kojoj je još otopljena paramagnetska tvar. Od šireg je značaja, jer se njome izbjegne kalibracija instrumenta, tehnika s dvije koncentrične cilindrične cjevčice: u jednoj se nalazi otapalo s označivačem, a u drugoj otopljena paramagnetska tvar s označivačem.

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Primljeno 3. srpnja 1968.