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Recent Advances in the Analysis of Surface-Active Agents by Non-Instrumental Methods

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THIS PAPER will deal with some of the recent advances in the non-instrumental analysis of surface-active agents. It will not presume to be an exhaustive compilation of all the recent advances in the field. The first portion of this paper will be devoted to applications of chromatography to the analysis of surface-active agents, the second portion will be devoted to the systematic detection of functional groups in surfactants by chemical means and the last portion to some recent chemical methods for the quantitative analysis of surface-active agents.

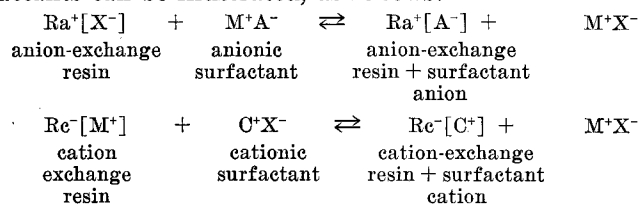
Chromatographic Methods

Recent applications of chromatography to the analysis of surface-active agents have developed along two major lines: 1) the use of ion-exchange resins to separate ionics from nonionics, and 2) the use of paper chromatography to separate and/or identify individual surfactants. There are a number of other applications for which chromatography has been used in this field, but the major efforts have been in the two directions mentioned. There are a number of sound reasons for this: The use of ion-exchange resins for the removal of ionic materials from nonionic is fundamentally a sounder approach than the use of nonionic adsorbents, such as silica gel, carbon, etc., which do not involve an ion exchange. The adsorption of an ionic surfactant by an ion exchange resin involves the exchange of an ion on the resin for a surfactant ion, and therefore the surfactant ion can be removed from the resin only by another, similarly-charged, ion. Washing with water or other solvents containing no ions cannot remove the surfactant ion from the resin. This is in contrast to adsorption on nonionic surfaces which do not involve ion exchange, where washing with a solvent may elute the adsorbed material. The numerous papers which have recently been published on the use of paper chromatography for the separation and/or identification of individual surfactants attest to the need that has existed for a convenient method for the separation and identification of homologs—

that is, surfactants having the same functional group but with hydrophobic groups of different length or structure. Very little work has been done in the past on this problem. The approach via paper chromatography is convenient and has a multitude of precedents in other fields. It may be used for samples as small as 1 µg and requires only the simplest apparatus.

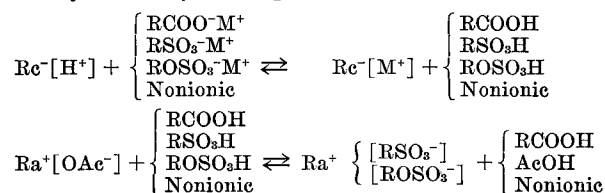
Ion Exchange

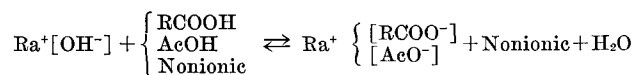
The principle involved in the use of ion exchange resins for the separation of nonionic and ionic surfactants can be illustrated, as follows:



The nonionic surfactant, having no ion to exchange with the resin, is not adsorbed by the resin and may be quantitatively recovered, unchanged, by washing the resin with an appropriate solvent.

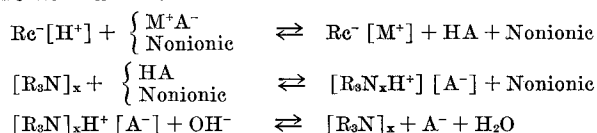
There are a number of ways in which this principle can be applied. Voogt (45) separates nonionics from soaps, sulfonates and alkyl sulfates by passing the mixture first through a column of cation-exchange resin in the H⁺ form to convert the carboxylates, sulfonates and sulfates to the corresponding free acids, then through an anion-exchange resin in the acetate form to adsorb the strongly acidic sulfonic and alkylsulfuric acids, and finally through an anion-exchange resin in the OH⁻ form to adsorb the carboxylic acids, leaving the nonionics in the filtrate.





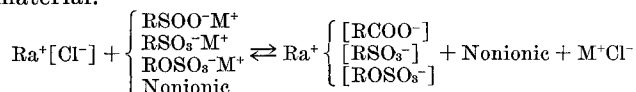
The sulfonates and alkyl sulfates are eluted from the acetate form anion-exchange resin with alcoholic hydrochloric acid and the carboxylates are eluted from the hydroxide form anion-exchange resin with hydrochloric acid in 1:1 alcohol-ether. The equivalents of strong acids (alkylsulfonic and alkylsulfuric) and carboxylic acids produced in the first exchange can be determined by potentiometric titration. A disadvantage of the method is that alkylsulfuric acids are not stable, and therefore alkyl sulfates cannot be analyzed reliably by this method.

Ginn and Church (12) separate anionic-nonionic mixtures by first also converting the anionics to the corresponding free acids by passing the mixture through a column of cation-exchange resin in the H^+ form, but they then pass it through a weakly basic anion-exchange resin in its un-ionized form to adsorb the anionic acids. The nonionics are unaffected and are found in the effluent.



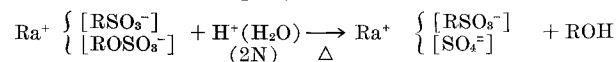
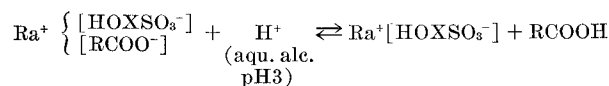
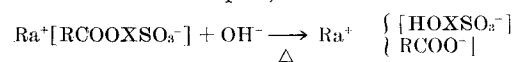
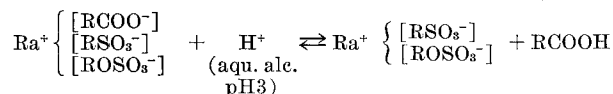
The surfactant anions are then eluted from the anion-exchange resins with alcoholic NaOH solution. This method is not suitable for materials which are unstable in strong acid or alkali, such as ester sulfonates, nonionic esters, and sulfated monoglycerides.

For my purposes, I prefer (37,38,40d) to use a batch technique for separating mixtures of ionics and nonionics, merely stirring a solution of the surfactants with a relatively small amount of the resin instead of percolating the solution over the resin held in a column. For separating mixtures of nonionics and anionics, I use a strong anion-exchange resin in the Cl^- form in neutral or weakly alkaline solution, thus avoiding hydrolysis of acid- or alkali-sensitive surfactants. After the mixture has been stirred with the resin for some time, the mixture is filtered and the resin is washed on the filter with alcohol to remove any adhering nonionic material.

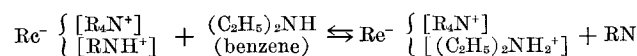
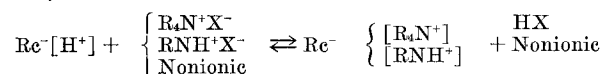


The anionic surfactants remain on the filter, adsorbed on the resin while the nonionics are found in the filtrate and washings, together with the inorganic salt which is produced in the exchange process. The nonionics are easily separated from this inorganic salt by extracting the residue from the filtrate and washings with an organic solvent such as acetone or chloroform in which the inorganic salt is insoluble. The various types of anionics adsorbed on the resin are then successively removed from the resin in the following manner:

The resin is first stirred with aqueous alcohol at a pH of about 3 to remove adsorbed carboxylates. Then the resin is heated with 5% KOH solution to saponify adsorbed ester-type anionics and their component parts are removed. Following this, the resin is heated with 2N hydrochloric acid to hydrolyze adsorbed sulfated anionics and their component parts are removed. Finally, the resin is heated with alcoholic hydrochloric acid to remove adsorbed sulfonates.



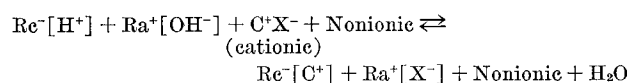
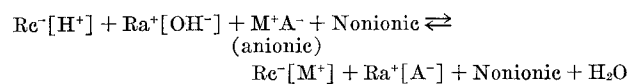
For separating mixtures of nonionics and cationics, I use a cation-exchange resin in the H^+ form and adjust the surfactant mixture to a pH of about 3, since almost all cationics are stable to cold, dilute acid. The preliminary steps of the procedure are similar to those for mixtures of anionics and nonionics. The mixture is stirred with the cation-exchange resin for some time, and then the mixture is filtered and the resin washed on the filter with alcohol to remove any adhering nonionics. The cationics remain on the filter, adsorbed on the resin.



Non-quaternary cationics and quaternary cationics are then removed successively from the resin, the former by stirring with a 10% solution of diethylamine in benzene, the latter by heating with alcoholic hydrochloric acid.

These procedures give quantitative recovery of the nonionic surfactants, but recovery of the ionic materials or their components averages only about 80%. However, the quality of the recovered ionics and their components is sufficiently good to permit identification of the individual ionic constituents of the mixture.

Ginn and Church (12) and Kilheffer and Jungermann (21) also use the batch technique to separate ionic from nonionic surfactants. Both sets of investigators use a mixture of a cation-exchange resin in the H^+ form and an anion-exchange resin in the OH^- form to remove the ionic surfactant and to permit the nonionic material to be obtained free of electrolyte in the filtrate. Ginn and Church use this technique to remove anionics from mixtures with nonionics; Kilheffer and Jungermann use it to remove cationics from their mixtures with polyoxyethylene glycols. This mixed-bed technique, however, cannot be used for surfactants which are sensitive to acid or alkali.



A few investigators have developed column chromatographic procedures for the separation of *nonionics from each other*, notably mixtures of ester-type nonionics by adsorption on silica gel and elution with solvents in order of increasing polarity. Ravin, Meyer and Higuchi (36), separated the components of mixtures containing mineral oil and mono-, di-, and tristearin by column chromatography, using silica gel as the adsorbent and eluting the mineral oil with 16% isopropyl ether in isoctane, the tristearin with

100% isopropyl ether, the distearin with 70% ethyl ether in isooctane and the monostearin with 20% absolute ethanol in isopropyl ether. Quinlan and Weiser (35) separated mono-, di-, and triglycerides on silica gel columns containing 5% water by eluting the triglyceride with benzene, the diglyceride with 10% ethyl ether in benzene, and the monoglyceride with ethyl ether. Papariello and co-workers (32) extended the work of Ravin and co-workers on glyceryl stearates to the separation of esters of ethylene glycol and polyethylene glycols. They developed two solvent systems for eluting the esters from the silica gel column, one for glyceryl and ethylene glycol esters, the second for polyethylene glycol esters. Their solvent system for glyceryl and ethylene glycol esters was essentially that of Ravin and co-workers, while their solvent system for polyethylene glycol esters was 12% methanol in isopropyl ether for eluting the diesters, 10% methanol in chloroform for eluting the monoesters, and 35% methanol in chloroform for eluting the polyethylene glycols.

Kelly and Greenwald (20), on the other hand, used adsorption on a silica gel column to separate the products of varying ethylene oxide content formed when octylphenol is reacted with 9.7 moles of ethylene oxide. By eluting with acetone-chloroform mixtures containing increasing amounts of acetone, they successively obtained products containing from two through eleven moles of ethylene oxide.

In my laboratory, we have been working on the development of general methods for separating nonionics from each other and from materials usually encountered with them, using both column and thin layer chromatography (TLC). Results will be forthcoming shortly.

TLC has been used by Privett and co-workers (34) to separate mono-, di-, and triglycerides, by Mangold and Kammereck (25) to separate a number of classes of surface-active agents, including amines, quaternary ammonium salts, alkyl sulfates and sulfonates, and alkyl phosphates, and by Gee (11) to analyze sucrose esters in mixtures containing sucrose and raffinose.

Paper Chromatography

The use of paper chromatography for the separation and/or identification of individual surfactants is the second area which has had a very rapid growth during the past few years. Holness and Stone (16) in 1955 used untreated paper to separate sulfated alcohols, while Franks (8), that same year, used paper impregnated with cetyl alcohol as the stationary phase and aqueous alcohol saturated with cetyl alcohol as the mobile phase to separate and identify alkyl sulfates, alkylaryl sulfonates, quaternary ammonium, and pyridinium salts. Since that time, numerous papers have been published using impregnated and non-impregnated paper to separate and/or identify surface-active agents. Borecky, in a recent series of papers, has developed methods for separating and identifying sulfated alcohols, alkylaryl sulfonates, and other anionics by chromatography on non-impregnated paper or paper impregnated with lauryl alcohol (3,4). He has also developed methods for identifying alkylarylsulfonates (6) and ethoxylated alkylphenols (5) by converting them to alkylphenols and then chromatographing the alkylphenols on paper impregnated with various substances. The alkylarylsulfonates are converted to alkylphenols by fusing them with KOH; the ethoxylated alkylphenols are converted by cleaving them with HI. Borecky & Gasparic

separate and identify polyethylene glycols and their monoethers (7) by converting them to their 3,5-dinitrobenzoate esters and chromatographing the esters on paper impregnated with dimethylformamide, formamide, or paraffin oil. Gasparic and Hanzlik (9) use paper impregnated with *n*-octyl alcohol to separate and identify various types of quaternary ammonium compounds, while Holness and Stone in a 1958 paper (15) used untreated paper for the same purpose. Laws and Hancock (24) have separated *n*-alkylbenzenesulfonates on untreated paper, while Tajiri (43) has separated and identified surfactants of all charge types (anionics, cationics, nonionics, and ampholytics) by paper chromatography. Ginn, Church, and Harris (13) have used paper chromatography to detect polyethylene glycols in mixtures with nonionics and to determine the amounts of each semiquantitatively, while Moyer and co-workers (29) have used this technique to analyze mixtures of trimethyl octadecylammonium chloride and dimethyl dioctadecylammonium chloride.

Gas Liquid Chromatography

Gas liquid chromatography (GLC) has not, to my knowledge, been used directly for the separation and identification of surface-active agents. The reason for this is the high polarity, and consequent low volatility, of almost all surface-active agents. However, a number of investigators have converted surfactants to more volatile derivatives and subjected these derivatives to analysis by GLC. Knight and House (23) in 1959 used 93% phosphoric acid to release the hydrophobic portions of a number of surfactant types, including alkylaryl sulfonates, alkyl sulfates, fatty acid amides, fatty acid esters and ethoxylated alkylphenols, and then analyzed these hydrophobic portions by gas chromatography. Jungermann and co-workers (17,18) have used this procedure to distinguish alkylbenzenesulfonates from different manufacturers, to study the effect of sulfonation conditions on the structure of the hydrophobic group, and to evaluate the effect of structural changes in the hydrophobic portion on detergency. Setzkorn and Carel (42) have used this same approach to develop a micro method for determining the isomer composition of the hydrophobic portion of alkylbenzenesulfonates. Beck, Jungermann, and Linfield (1) have used GLC to identify soapstocks by converting them to their methyl esters, Metcalfe (28) has used this technique to analyze the hydrophobic portions of quaternary ammonium compounds by decomposing them to tertiary amines on alkaline columns, Kirkland (22) has analyzed sulfonic acids by converting them to their methyl esters, while McInnes and co-workers (26) have analyzed monoglycerides by converting them to their allyl esters. Blakey and Thomas (2) have used GLC to separate and identify the components of commercial linear alkylbenzenes while Nakagawa and co-workers (31) have used it to determine impurities in nonionic surfactants.

Other papers dealing with the analysis of surfactants by various chromatographic techniques include a recent paper by Keily and co-workers (19) on the use of salting out chromatography to separate mixtures of toluenesulfonates, xylenesulfonates, and long-chain alkylbenzenesulfonates, one by Mysels and co-workers (30) on the separation of alkylbenzenesulfonates by adsorption on charcoal, and a paper by Metcalfe (27) on the determination of quaternary ammonium compounds by the use of cellulose ion exchange resin.

TABLE I
Classification of Surfactants by Elements (40b)

Class	Elements
IA	No "additional elements" (nitrogen, sulfur, phosphorus or metal) present
IB	Metal as the only "additional element"
IIA	Sulfur as the only "additional element"
IIB	Sulfur and metal as the only "additional elements"
IIIA	Nitrogen as the "additional element" (with or without X ⁻ , HSO ₄ ⁻ , SO ₄ ²⁻ , H ₂ PO ₄ ⁻ , HPO ₄ ²⁻ or PO ₄ ³⁻)
IIIB	Nitrogen and metal as the only "additional elements"
IVA	Nitrogen and organic sulfur as the only "additional elements"
IVB	Nitrogen, sulfur and metal as the "additional elements"
VA	Phosphorus as the only "additional element"
VB	Phosphorus and metal as the only "additional elements"
VC	Nitrogen and organic phosphorus as the "additional elements"

Systematic Detection of Functional Groups

Up to the rather recent past, the structural identification of surface-active agents was in a fairly chaotic condition, with numerous empirical tests, many of which were non-specific and quite unreliable, being suggested for identifying surfactants. A few years ago, I attempted to bring some order into this area by initiating a program whose aim was to develop sensitive and specific tests for all the functional groups present in surface-active agents in current use, and then to work them into systematic schemes for elucidating the structures of these materials. The procedures which were developed were published in book form in 1960 (40c). I would like to show the scope of these functional group tests and to illustrate their application by giving an example of how they are used to analyze one class of surfactants.

The first step in the elucidation of the structure of an unknown surfactant, as in the structural analysis of any organic compound by chemical means, is to subject it to a qualitative elemental analysis for N, S, P, halogens, and metal ions. Based on this elemental analysis, the surfactant can be placed in one of the classes listed in Table I. The surfactant is then subjected to a series of tests in systematic fashion to detect the functional groups in it. A different scheme of analysis is used for each of the classes based on elemental analysis, since the functional groups possibly present obviously vary with the elemental composition of the surfactant.

TABLE II
Groups Detected in Analysis for Functional Groups (39)

Aromatic nucleus	Ar-
Carboxylate	-COO ⁻
Ester	-COOR
Glucoside	-CH(OH)OR
Glyceride	ROCH ₂ CH(OR')CH ₂ OR"
Naphthenic acid	ArOH
Phenol	-CH ₂ CH ₂ O _x
Polyoxyethylene	-CH(CH ₂)CH ₂ O _x
Polyoxypropylene	
Rosin Derivative	
Tertiary acetylenic glycol	R ₁ R ₂ C(OH)C≡CC(OH)R ₃ R ₄
Unsaturation	-C=C-
Alkyl sulfate	ROSO ₃ O-
Aryl sulfonate	ArSO ₃ O-
Organic sulfate	-OSO ₃ O-
Amide	-CON<
β-Hydroxyamine	>C-C< NH ₂ OH
β-Hydroxyethylamine	>NCH ₂ CH ₂ OH
Polypeptide	-[NHCOCH(R)NHCOC(H)R] _x
Pyridinium, quinolinium or isoquinolinium quaternary	[R-C ₅ H ₄ N-R'] ⁺
Quaternary ammonium	[R ₁ R ₂ R ₃ R ₄ N] ⁺
Tetraalkylammonium quaternary with <26 carbon atoms	
Tetraalkylammonium quaternary with >25 carbon atoms	
Trialkylamine Oxide R ₁ R ₂ R ₃ NO	

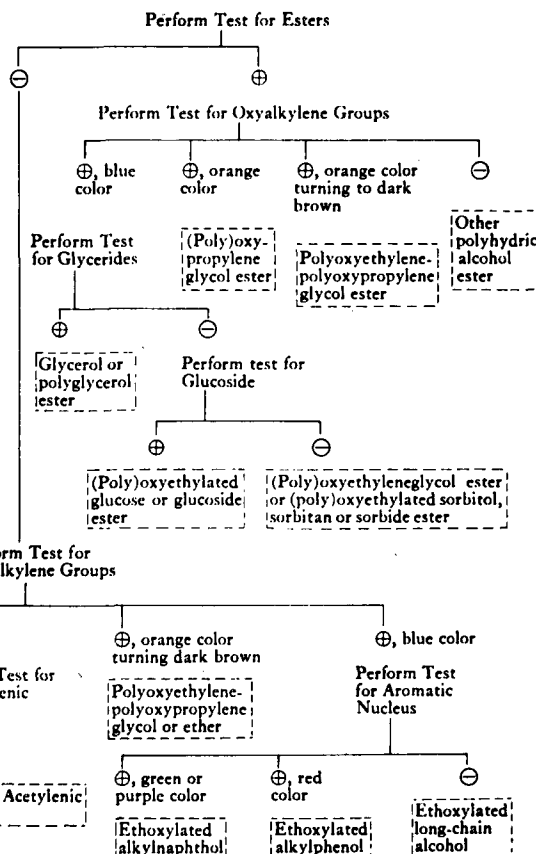


FIG. 1. Analysis of surfactant containing no N, S, P or metal (40a).

A list of the functional groups which can be detected in this analysis for functional groups is given in Table II. The tests which are used to detect these functional groups are sensitive and specific tests, performed on a semi-micro scale, mostly new tests developed especially for this purpose. However, they do include some tests which have been used for many years, and which we have found suitable for this work.

The manner in which these functional group tests are combined to elucidate the structure of the unknown surfactant in a systematic fashion is illustrated by the example in Figure 1, which shows the procedure for analyzing a surfactant containing no N, S, P, or metal ions. Different schemes of this type are used to analyze surfactants in all the other classes based on elemental analysis.

Quantitative Methods

A few of the recent methods for the quantitative determination of surfactants are included. One is a method for determining the total number of equivalents of anionic or of cationic present in a composition by passing it through a cation exchange resin in the H⁺ form and titrating the eluted H⁺ with standard alkali. This method was used by Takahama and Nishida (44) to determine the number of equivalents of anionic present in mixtures with nonionics and by Russell and Whittaker (41) to determine the equivalent weights of both cationic and anionic surfactants.

Another recent quantitative method is that of Pitter (33), who has developed a new colorimetric method for the determination of ethoxylated nonionics at low concentration, based upon the commonly-used precipitation reaction with Ba²⁺ and phosphotungstic acid in acid medium. The barium-phosphotungstic acid-

surfactant complex is precipitated in the usual manner and is then dissolved in concentrated sulfuric acid. The addition of hydroquinone to this solution produces a red color, due to soluble tungstate, which is measured at 500 $\mu\mu$. Anionics which form precipitates with BaCl_2 interfere, as do substances, such as proteins and cationics, which form complexes with heteropoly acids.

Gatewood and Graham (10) have developed a method of assaying sorbitol esters by saponifying them first to release the sorbitol, then oxidizing the sorbitol with periodate, coupling the formic acid produced in this oxidation with chromotropic acid, and measuring the resulting wine color at 570 $\mu\mu$.

Finally, Hill and co-workers (14) have improved the methylene blue method for determining alkylbenzenesulfonates in water supplies by using a chromic-sulfuric acid mixture to oxidize interfering substances, such as organic sulfates and phosphates. Under the conditions of the procedure, the alkylbenzenesulfonate is unaffected by the oxidation mixture.

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Principles and Utility of Nuclear Magnetic Resonance in Structure Determination of Surfactant Chemicals

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THE THEORETICAL basis for the phenomenon of nuclear magnetic resonance (NMR) has been understood for some 17 years now since the original experiments by Purcell, Torrey and Pound (1) at Harvard and by Bloch, Hansen, and Packard (2) at Stanford University were first published in 1946. In the intervening years, the technique of high-resolution nuclear magnetic resonance has evolved into a research tool of rapidly increasing importance to chemists. It is only within the last three years, however, that sufficiently reliable commercial instrumentation has become available so that NMR can now be considered practical as a routine analytical tool.

The Principle

The information which can be gained by this method is ideally suited for determination of average molecular structures for a variety of raw materials, intermediates, and products in the area of surfactant chemicals. Since the physical and functional properties of these materials are determined primarily by their molecular structures, NMR provides the detergent chemist a unique method of gaining insight into the basic nature of the molecules with which he deals. The purpose of this discussion is to describe some of these areas in which NMR has proven particularly useful. The discussion will be divided into two parts. In the present paper, a general review of the basic principles of the technique

will be given. The emphasis will be on application as a general tool for qualitative and quantitative analysis and structure determination of hydrogen-containing molecules. In a second paper, the application of the NMR method to specific problems of structure in the area of surfactant chemicals will be discussed and illustrated by several examples of applications which have been made in our laboratories, some of which have been described elsewhere (3,4). Those who wish to go more deeply into the subject are referred to several excellent books which treat the theory with varying degrees of sophistication (5, 6,7,8,9,10).

The Principle of NMR Measurements

A. *Background*—All atoms whose nuclei contain odd numbers of protons or neutrons possess the property of nuclear spin, which makes their nuclei behave somewhat similar to very small spinning magnets. Actually, these magnetic nuclei obey the laws of quantum physics rather than classical physics, but the analogy is close enough for a working comparison.

The most common examples of nuclei which can be studied by using this property are ^1H , ^{19}F , ^{31}P , ^{11}B and ^{13}C . Atoms with an even number of protons and neutrons— ^{12}C and ^{16}O , for example—do not exhibit magnetic properties. Unless otherwise stated, further comments will refer only to the hydrogen