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SUMMARIES FOR CARD INDEXES

Reactions of metallochromic indicators on micelles—I: General observations: V. Svoboda and V. Chromý, *Talanta*, 1965, **12**, 431. (Institute of Pure Chemicals, Brno, Czechoslovakia.)

Summary—Purple-red alkaline solutions of Xylenol Orange are decolourised by the addition of cationic long-chain quaternary salts. A definite minimal ratio of the detergent to the indicator is necessary to bring about the full decolourising effect. The formation of micellar aggregates is supposed. In these one dye molecule is surrounded by at least five molecules of cetylpyridinium bromide and six molecules of cetyltrimethylammonium bromide, respectively. According to absorption spectra, the electronic structure of the Xylenol Orange in this state is that normally found at pH 6.4. Xylenol Orange, bounded in these aggregates, is capable of forming coloured complexes with a number of cations over a wider pH range than usual. Some ions, such as calcium and magnesium, not usually determined complexometrically with Xylenol Orange as an indicator may be successfully titrated using the modified indicator.

Reactions of metallochromic indicators on micelles—II: Application of Xylenol Orange to complexometric titrations in an alkaline medium: V. Chromý and V. Svoboda, *Talanta*, 1965, **12**, 437. (Institute of Pure Chemicals, Brno, Czechoslovakia)

Summary—Xylenol Orange in the presence of cetylpyridinium bromide has been applied as a metallochromic indicator for the complexometric determination of some metal cations in an alkaline medium. Precise successive determinations of some pairs of metals in the same solution are possible.

Reflectance spectra of two solvated uranium 8-hydroxyquinolates: R. J. Magee and Louis Gordon, *Talanta*, 1965, **12**, 441. (Department of Chemistry, Case Institute of Technology, Cleveland, Ohio 44106, U.S.A.)

Summary—On precipitation of uranyl 8-hydroxyquinolate from homogeneous solution, two different chelates are obtained.

$$UO_2(C_9H_6NO)_2\cdot C_9H_6NOH$$

is dark red whereas $[UO_2(C_9H_6NO)_2]_2\cdot C_9H_6NOH$ is orange. On grinding, the dark-red chelate becomes orange. Reflectance spectra are used to explain the initial colour difference as well as the change in colour of the dark-red compound to orange on grinding.

РЕАКЦИИ МЕТАЛЛОХРОМНЫХ ИНДИКАТОРОВ НА МИЦЕЛЛЯХ—I: ОБЩИЕ НАБЛЮДЕНИЯ:

V. Svoboda and V. Chromý, *Talanta*, 1965, **12**, 431.

Резюме—Шелочные растворы ксиленолоранжевого, обладающие пурпурным цветом обесцвечиваются добавлением катионоактивных четвертичных солей с длинной цепью. Нужно достигнуть определенное минимальное отношение детержента и индикатора чтобы полностью получился эффект обесцвечивания. Предполагается образование мицеллярных аггрегатов. В этих аггрегатах каждая молекула красителя окружена с не меньше чем пятми молекулами бромида цетилпиридиния и шестми молекулами бромида цетилтриметиламмония, соответственно. Спектры светопоглощения показывают что электронная структура ксиленолоранжевого в этом состоянии соответствует структуры, которая обычно наблюдается при pH 6·4. Ксиленолоранжевый в форме этих аггрегатов образует окрашенные комплексы с рядом катионов в области pH шире чем обыкновенно. Некоторые ионы, как на пример кальций и магний, которые как правило не определяют ксиленолоранжевым в качестве индикатора, можно удачно титровать с использованием модифициранного индикатора.

РЕАКЦИИ МЕТАЛЛОХРОМНЫХ ИНДИКАТОРОВ НА МИЦЕЛЛЯХ—II: ИСПОЛЬЗОВАНИЕ КСИЛЕНОЛОРАНЖЕВОГО ПРИ КОМПЛЕКСОМЕТРИЧЕСКИХ ТИТРОВАНИЯХ В ЩЕЛОЧНОЙ СРЕДЕ:

V. Chromý and V. Svoboda, *Talanta*, 1965, **12**, 437.

Резюме—Ксиленолоранжевый в присутствии бромида цетилпиридиния использован в качестве металлохромного индикатора для комплексометрического определения некоторых катионов в щелочной среде. Удалось провести весьма точные последовательные определения некоторых пар металлов в одном и том же растворе.

РЕФЛЕКСНЫЕ СПЕКТРЫ ДВУХ СОЛЬВАТИРОВАННЫХ 8-ГИДРОКСИХИНОЛАТОВ УРАНА:

R. J. Magee and Louis Gordon, *Talanta*, 1965, 12, 441.

Резюме—При осаждении 8-гидроксихинолатов уранила из гомогенных растворов получают два различных комплекса.

$$UO_2(C_9H_6NO)_2\cdot C_9H_6NOH$$

темнокрасного, а $[UO_2(C_9H_6NO)_2]_2\cdot C_9H_6NOH$ оранжевого цвета. При дроблении темнокрасный комплекс становится оранжевым. На основании рефлексных спектров объясняют начальную разницу окраски и изменение окраски комплекса из темнокрасной в оранжевую при дроблении.

Infrared spectra of chelate compounds—IV: A study of the uranyl chelates of 8-hydroxyquinoline in the region 5000—250 cm^{-1}: R. J. Magee and Louis Gordon, *Talanta*, 1965, **12,** 445. (Department of Chemistry, Case Institute of Technology, Cleveland, Ohio, 44106, U.S.A.)

Summary—Previous investigations have shown that two different uranium chelates of 8-hydroxyquinoline can be precipitated from homogeneous solution. Dark red $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$ is obtained at pH 5·0 and orange $[UO_2(C_9H_6NO)_2]_2 \cdot C_9H_6NOH$ at pH 6·8; the *normal* chelate $UO_2(C_9H_6NO)_2$ is green. The infrared spectra of the solvated compounds have been examined in the range 5000–250 cm^{-1} and that of the normal chelate in the range 5000–650 cm^{-1}. From this it is concluded that the solvated chelates have very similar structures.

The oximation of biacetyl: Orviille E. Hileman, Jr. and Louis Gordon *Talanta*, 1965, **12,** 451. (Department of Chemistry, Case Institute of Technology, Cleveland, Ohio 44106, U.S.A.)

Summary—Spectrophotometric evidence indicates that the reaction of biacetyl with hydroxylamine proceeds through the formation of two carbinolamine intermediates. The second of these intermediates is also encountered in the reaction of biacetyl monoxime with hydroxylamine. The rate-limiting step in the oximation of biacetyl is the slow dehydration of the initially formed intermediate, as is evidenced from the various rate constants obtained for the two reactions over the range 0–10°. When nickel(II) is present in the biacetyl-hydroxylamine system, the formation of nickel dimethylglyoximate proceeds by two independent mechanisms, whereas only a single mechanism is responsible for precipitate formation in the biacetyl monoxime-hydroxylamine system.

Spectrophotometric determination of copper with polyaminocarboxylic acids: Ethylenediamine-N,N′-di-α-propionic acid: J. J. R. F. Da Silva, J. C. G. Calado and M. L. De Moura, *Talanta*, 1965, **12,** 467. [Centro de Estudos de Química Nuclear (I.A.C.) Instituto Superior Técnico, Lisboa-1, Portugal.]

Summary—A new method for the spectrophotometric determination of copper with polyaminocarboxylic acids is presented. The ligand chosen is ethylenediamine-N,N′-di-α-propionic acid (EDDPA) which compares favourably, in sensitivity and selectivity, with all the other similar compounds previously proposed. The copper complex absorbs at 670 mμ with a molar extinction coefficient of 140 at any pH between 3 and 8. Beer's law is obeyed over the range 0–400 ppm of copper and the temperature and ionic strength do not adversely affect the method. Nickel interferes when present in comparable or greater amounts than copper.

СПЕКТРЫ ПОГЛОЩЕНИЯ КОМПЛЕКСОВ В ИНФРАКРАСНОЙ ОБЛАСТИ. ИЗУЧЕНИЕ КОМПЛЕКСОВ УРАНИЛА С 8-ГИДРОКСИХИНОЛИНОМ В ОБЛАСТИ 5000 СМ$^{-1}$ ДО 250 СМ$^{-1}$:

R. J. MAGEE and LOUIS GORDON, *Talanta*, 1965, **12**, 445.

Резюме—Прежние исследования показали что при осаждении из гомогенных растворов получают два различных комплекса урана. $UO_2(C_9H_6NO)_2.C_9H_6NOH$ темнокрасного цвета осаждается при pH 5,0 а $[UO_2(C_9H_6NO)_2]_2.C_9H_6NOH$ оранжевого цвета при pH 6,8; "нормальный" комплекс $UO_2(C_9H_6NO)_2$ зеленый. Инфракрасные спектры сольватированных комплексов и 8-гидроксихинолина исследованы в области 5000–250 см$^{-1}$, а спектр нормального комплекса в области 5000–650 см$^{-1}$. На основании этих данных сделан вывод что комплексы имеют очень похожую структуру.

ОКСИМИРОВАНИЕ БИАЦЕТИЛА:

ORVILLE E. HILEMAN, JR., and LOUIS GORDON, *Talanta*, 1965, **12**, 451.

Резюме—Спектрофотометрическое исследование указивает, что реакция биацетила с гидроксиламином переходит через формирование двух промежуточных карбиноламинов. Второе от этих промежуточных соединений встречается тоже в реакции моноксима биацетила с гидроксиламином. Скорость оксимирования биацетила зависит от медленной дегидратации первоначально образованного промежуточного соединения, как видно из разницы между константами скорости реакции этих реакций в области 0–10°C. Если никель(II) присутствует в системе биацетил—гидроксиламин, образование диметилглиоксимата никеля следит два независимых механизма, тогда как только один механизм ответственный для образования осадка в системе моноксим биацетила—гидроксиламин.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ МЕДИ КОМПЛЕКСОНАМИ: ЭТИЛЕНДИАМИН-N,N'-ДИ-АЛЬФА-ПРОПИОНОВАЯ КИСЛОТА:

J. J. R. FRAUSTO DA SILVA, J. C. GONÇALVES CALADO and M. LEGRAND DE MOURA, *Talanta*, 1965, **12**, 467.

Резюме—Разработан новый метод для колориметрического определения меди комплексонами. Выбранный лиганд была этилендиамин-И,И'-ди-альфа-пропионовая кислота (ЭДДПА), которая обладает хорошой чувствительностью и избирательностью в сравнении с раньше предложенными комплексонами. Комплекс меди с ЭДДПА показывает максимум поглощения при 670 имк с $\varepsilon_{\text{макс}} = 140$, в области pH 3–8. Экстинкция следит закон Беера в области 0–400 мкг Cu^{2+}/мл; температура и ионная концентрация не имеют вредного влияния на метод. Никель мешает если присутствует в концентрации ровной или больше чем концентрация меди.

Contributions to the basic problems of complexoemtry—XIX: Determination of zinc and cadmium: β-Mercaptopropionic acid as a masking reagent for cadmium: R. PŘIBIL and V. VESELÝ, *Talanta*, 1965, **12**, 475. (Laboratory for Analytical Chemistry, Polarographic Institure of J. Heyrovský, Czechoslovak Academy of Sciences, Prague, Jilská 16, Czechoslovakia.)

Summary—A new method for the successive determination of zinc and cadmium (in the presence of copper) is described. It is based on the masking of cadmium (copper) with β-mercaptopropionic acid (MPA) and followed by direct titration of zinc with triethylenetetraminehexa-acetic acid (TTHA). After the addition of DCTA cadmium is determined indirectly by back-titration with zinc nitrate solution. All titrations are carried out with Xylenol Orange as indicator in a slightly acid medium, where alkaline earth metals are without effect on the results.

Behaviour of silver(II) in phosphoric acid media and a general mechanism for solvent oxidation: G. A. RECHNITZ and S. B. ZAMOCHNICK, *Talanta*, 1965, **12**, 479. (Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, U.S.A.)

Summary—A spectrophotometric investigation of silver(II) in phosphoric acid solution has revealed the presence of two predominant silver(II) phosphate complexes, which undergo reduction by water according to a rate law second order in silver(II), inverse first order in silver(I) and complex in solvent anion and hydrogen ion concentrations. A comparison of trends in molar absorptivities and pseudo-first order rate constants indicates that the reduction step is preceded by rapid equilibria involving silver(II) complexes. A single oxidation-reduction mechanism seems to be common to the three acidic media studied to date.

Potentiometric determination of N-substituted dithiocarbamates: *A. HULANICKI and L. SHISHKOVA, Talanta, 1965, **12**, 485. (Department* of Inorganic Chemistry, University, Warsaw, Poland.)

Summary—A simple and general method for the determination of *N*-substituted dithiocarbamates is described. The sample, dissolved in water, is decomposed with a known amount of acid and the solution is back-titrated with standard base. The number of equivalents of dithiocarbamate (as CS_2^- groups) is easily found from the titration curves.

ВКЛАД В ОСНОВНЫЕ ПРОБЛЕМЫ КОМПЛЕКСОМЕТРИИ—XIX: ОПРЕДЕЛЕНИЕ ЦИНКА И КАДМИЯ. ПРИМЕНЕНИЕ БЕТА-МЕРКАПТОПРОПИОНОВОЙ КИСЛОТЫ КАК МАСКИРУЮЩЕГО АГЕНТА ДЛЯ КАДМИЯ:

R. Přibil and V. Veselý, *Talanta*, 1965, **12**, 475.

Резюме—Описан новый метод для последовательного определения цинка и кадмия (тоже в присутствии меди). Метод основан на маскировании кадмия (или меди) с бета-меркаптопропионовой кислотой и последовательным прямым титрованием цинка с ТТХА. После добавления ДЦТА кадмий определяют косвенно, обратным титрованием с раствором нитрата цинка. Все титрации проводят с ксиленолоранжем как индикатором в слабокислой среде, где щелочноземельные элементы не имеют влияния на результаты.

ПОВЕДЕНИЕ СЕРЕБРА (II) В ФОСФОРНОКИСЛЫХ СРЕДАХ И ОБЩИЙ МЕХАНИЗМ ОКИСЛЕНИЯ РАСТВОРИТЕЛЯМИ:

G. A. Rechnitz and S. B. Zamochnick, *Talanta*, 1965, **12**, 479.

Резюме—Спектрофотометрическое исследование серебра(II) в фосфорнокислом растворе обнаружило существование двух преобладающих комплексов фосфата серебра(II), которые восстанавливаются с водой, следя реакцию второй степени в отношении на серебро(II), обратной первой степени в отношении на серебро(I) и образуя комплексы в отношении на концентрацию анионов растворителя и ионов водорода. Сравнение направления молярных поглотительностей и констант скорости реакции псевдо-первой степени показывает что восстановлению предшествует быстрое равновесие комплексов серебра(II). Кажется что тот же самый окислительно—восстановительный механизм существует в тех трех кислых средах, которые исследованы до сих пор.

ПОТЕНЦИОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ *N*-ЗАМЕЩЕННЫХ ДИТИОКАРБАМАТОВ:

A. Hulanicki and L. Shishkova, *Talanta*, 1965, **12**, 485.

Резюме—Описан несложный и общеприменимый метод для определения *N*-замещенных дитиокарбаматов. Растворенную в воде пробу разлагают с известным количеством кислоты и избыток кислоты титруют стандартным раствором щелочи. Число эквивалентов дитиокарбамата (в виде группы CS_2^-) легко вычисляется из кривых титрования.

A simple computer circuit for automatic spectrophotometric analysis of binary mixtures by differential reaction rates: DANIEL PINKEL and HARRY B. MARK, JR., *Talanta*, 1965, **12**, 491. (Department of Chemistry, University of Michigan, Ann Arbor, Michigan, U.S.A.)

Summary—A simple analogue computer circuit, for application with a continuous reading spectrophotometer to give automatic analysis of binary mixtures of closely related substances using a differential reaction rate technique, is described. The circuit solves the simultaneous equations of the Method of Proportional Equations for the concentrations of the components in the mixture. The method is useful for first- or pseudo-first order competitive reactions. A timing circuit automatically supplies the absorbance (converted as described from the transmittance) of the reacting solution at two chosen times during the reaction, to the computer. The output voltages are adjusted within the circuit to read directly in units of concentration.

Determination of aminoalkylthiophosphorus compounds and thiols with palladium(II) ions as the reagent: HERMAN HAGLUND and INGER LINDGREN, *Talanta*, 1965, **12**, 499. (Research Laboratory, Mo och Domsjö AB, Örnsköldsvik, Sweden.)

Summary—Two methods of determination based on the reactions of the palladium(II) ion with thiol compounds, thiocholine esters and thiophosphorus compounds are described. One of the methods is photometric, and the substance measured is the palladium-thiol complex formed when palladium chloride is added to a solution of a thiocholine ester or a thiophosphorus compound. The second method, used for the determination of thiol compounds, is titrimetric, with a palladium chloride solution as the titrant.

НЕСЛОЖНАЯ ЦЕПЬ СЧЁТЧИКА ДЛЯ АВТОМАТИЧЕСКОГО СПЕКТРОФОТОМЕТРИЧЕСКОГО АНАЛИЗА ДВОЙНЫХ СМЕСЬ ПРИ ПОМОЩИ ДИФФЕРЕНЦИАЛЬНЫХ СКОРОСТЕЙ РЕАКЦИИ:

DANIEL PINKEL and HARRY B. MARK, JR., *Talanta*, 1965, **12**, 491.

Резюме—Описана несложная цепь аналог-счётчика, которая в связи с непрерывным самопишущим спектрофотометром дает возможность автоматического анализа двойных смесь сродных веществ с использованием техники дифференциальных скоростей реакции. Цепь решает одновременные уравнения Метода Пропорциональных Уравнений для концентрации компонентов в смесе. Метод полезен для конкурирующих реакций первого и псевдопервого порядка. Цепь для регистрации времени автоматически подает счётчику светопоглощение реагирующего раствора (получено как указано из пропускания света) в двух выбранных моментах в течении реакции. Выходное напряжение регулировано в цепи таким образом чтобы выражать единици концентрации.

ОПРЕДЕЛЕНИЕ АМИНОАЛКИЛТИОФОСФОРНЫХ СОЕДИНЕНИЙ И ТИОЛОВ С ИОНОМ ПАЛЛАДИЯ (II) В КАЧЕСТВЕ РЕАГЕНТА:

HERMAN HAGLUND and INGER LINDGREN, *Talanta*, 1965, **12**, 499.

Резюме—Описаны два метода которые основываются на реакциях иона палладия(II) с тиолами, тиохолиновыми эфирами и тиофосфорными соединениями. Первый метод фотометрический: он определяет тиоловый комплекс палладия, который образуется когда хлорид палладия добавляется раствору тиохолинового эфира или тиофосфорного соединения. Второй метод титриметрический для определения тиоловых соединений, с использованием раствора хлорида палладия в качестве титранта.

Liquid–liquid, discontinuous, counter-current solvent extraction for determination of trace constituents in geological materials-I: Extraction with solvents lighter than water: R. R. Brooks, *Talanta*, 1965, **12,** 505. (Department of Chemistry and Biochemistry, Massey University, Palmerston North, New Zealand.)

Summary—A new analytical technique for the determination of trace constituents in silicate rocks has been developed. This consists of the use of liquid–liquid, discontinuous, counter-current, solvent extraction in which the chloro-complexes of a number of elements are extracted into a ketonic solvent. Extraction into methyl isobutyl ketone is followed by spectrographic analysis of the contents of the individual extraction tubes, from which a series of extraction curves is plotted. These curves show that trace constituents of a silicate rock can be separated from the main constituents and can be fractionated from each other. By the use of a solution of a granite-gneiss in $3M$ hydrochloric acid and varying concentrations of this ligand as the aqueous phase in the extraction train, it is shown that a number of trace constituents can be isolated and hence enriched from the rock solution. The method appears to have the advantages of speed, flexibility, relative freedom from contamination and the fact that even weakly-extracted elements may be determined quantitatively. It is suggested that the technique may be suitable not only for the analysis of trace constituents in silicate rocks, but also as a separation method in radioactivation analysis. A further application may be the separation of different oxidation states of the same element, *e.g.*, antimony(III) from antimony(V).

ОБЗОР ВОЗМОЖНОСТЕЙ МЕТОДА ЖИДКОФАЗНОЙ, ПРЕРЫВНОЙ, ПРОТИВОТОЧНОЙ ЭКСТРАКЦИИ РАСТВОРИТЕЛЯМИ ДЛЯ ОПРЕДЕЛЕНИЯ СЛЕДОВЫХ КОМПОНЕНТОВ В ГЕОЛОГИЧЕСКИХ ВЕЩЕСТВАХ—I:

R. R. Brooks, *Talanta*, 1965, **12**, 505.

Резюме—Разработан новый аналитический метод для определения следовых количеств элементов в силикатных породах. Метод основывается на жидкофазной, противоточной прерывной экстрацкии хлорокомплексов ряда элементов с использованием кетонового растворителя. После экстракции метилизобутилкетоном проведен спектрохимический анализ содержания индивидуальных экстракционных трубок, на основании которого нанесена серия кривых экстракции. Эти кривые показивают что удается разделять следовые компоненты силикатной породы от главных компонентов, также как и одного элемента от другого. Пользуясь раствором гнейсогранита в 3N соляной кислоте и различными концентрациями этого лиганда в качестве водной фазы в экстракционной установке получено изолирование и этим путем обогащение ряда следовых элементов из раствора породы. Кажется что метод быстрый, приспособляемый и относительно свободный от помех; даже слабо экстрагирующиеся элементы определяются количественно. Описана процедура предлагается не только для анализа следовых элементов в силикатных породах но и в качестве сепарационного метода в радиоактивационном анализе. Кроме того методом можно пользоваться для разделения различных степеней окисления одного и того же элемента, как на пример сурьмы(III) от сурьмы(V).

Liquid-liquid, discontinuous, counter-current solvent extraction for determination of trace constituents in geological materials-II: Extraction with solvents heavier than water: R. R. Brooks, *Talanta*, 1965, **12,** 511. (Department of Chemistry and Biochemistry, Massey University, Palmerston North, New Zealand).

Summary—A new analytical technique has been developed for the determination of trace elements in sea water and other natural waters. The method consists of the use of liquid-liquid, counter-current, solvent extraction with solvents heavier than water. Relatively large volumes of sea water form the moving aqueous layer in the extraction procedure, whereas the lower stationary layer comprises the chelating agents dithizone or 8-hydroxyquinoline dissolved in carbon tetrachloride and chloroform, respectively. Elements are progressively absorbed from the sea water as the aqueous layer passes along the extraction train. Trial experiments with sea water containing additives shows that solutions of 8-hydroxyquinoline and to a lesser extent dithizone are capable of quantitatively retaining a number of elements in a small number of extraction tubes. An experiment has been carried out with a sample of pure sea water from which Mn, Pb, Mo, Sn, Ni, Al, V, Ag, Zn and La were quantitatively extracted into a solution of 8-hydroxyquinoline in chloroform; the elements were all determined spectrographically. It is considered that the method should have wide applications in the analysis of trace elements in sea water because enrichment factors of 400,000 are obtained for the concentrations of these elements. The technique is simple and comparatively free from contamination dangers.

Spectrofluorimetric determination of microgram amounts of thallium: G. F. Kirkbright, T. S. West and C. Woodward, *Talanta*, 1965, **12,** 517. (Department of Chemistry, Imperial College, London S.W.7, England.)

Summary—Thallium(I) in a concentrated hydrochloric acid-potassium chloride medium shows a violet fluorescence with an excitation maximum at 250 $m\mu$ and a fluorescence emission maximum at 430 $m\mu$. This has been applied for the spectrofluorimetric determination of thallium down to the range 0·01 to 0·08 ppm. The interference of 53 ions has been examined at the 100-fold molar excess level. Hydrogen peroxide oxidation to thallium(III) and extraction from $1{\cdot}5M$ hydrochloric acid into diethyl ether, followed by sulphur dioxide reduction, separates microgram amounts of thallium quantitatively from all interfering cations investigated except antimony(V), bismuth, gold and platinum(IV). Large amounts ($\times 10^6$) of sulphate do not interfere.

ОБЗОР ВОЗМОЖНОСТЕЙ МЕТОДА ЖИДКОФАЗНОЙ, ПРЕРЫВНОЙ, ПРОТИВОТОЧНОЙ ЭКСТРАКЦИИ РАСТВОРИТЕЛЯМИ ДЛЯ ОПРЕДЕЛЕНИЯ СЛЕДОВЫХ КОМПОНЕНТОВ В ГЕОЛОГИЧЕСКИХ ВЕЩЕСТВАХ—II: ЭКСТРАКЦИЯ С РАСТВОРИТЕЛЯМИ ТЯЖЕЛЕЕ ВОДЫ:

R. R. Brooks, *Talanta*, 1965, **12**, 511.

Резюме—Разработан новый аналитический метод для определения следовых количеств элементов в морской воде и других природных водах. Метод основывается на жидкофазной противоточной экстракции с использованием растворителей тяжелее воды. В экстракционной процедуре двигающийся водный слой образован от относительно большего объема морской воды, тогда как нижный неподвижный слой представляет раствор комплексообразных агентов дитизона или оксина в тетрахлорметане или хлороформе. Элементы прогрессивно абсорбируются из морской воды с продвижением водного слоя через экстракционную установку. Опыты с морской водой, содержающой присадки показали, что растворы оксина—и в меньшей мере дитизона—могут задержать ряд элементов в небольшом числе экстракционных трубок. В одном опыте из пробы чистой морской воды количественно экстрагированы раствором 8-оксихинолина в хлороформе Mn, Pb, Mo, Sn, Ni, Al, V, Ag, Zn, и La. Все элементы определены спектрохимическим методом. Считается что этим методом можно широко пользоваться для анализа следовых элементов в морской воде, с тех пор как получается 400.000-кратно обогащение этих элементов. Метод является несложным и свободным от помех. Предлагается его применение в радиоактивационном анализе.

СПЕКТРОФЛУОРИМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ МИКРОГРАММОВЫХ КОЛИЧЕСТВ ТАЛЛИЯ:

G. F. Kirkbright, T. S. West and C. Woodward, *Talanta*, 1965, **12**, 517.

Резюме—Таллий (I) в растворе содержающем сильную солляную кислоту и хлорид калия показывает фиолетовую флуоресценцию с максимумом возбуждения при 250 ммк и максимумом флуоресцентной эмиссии при 430 ммк. Эти максимуми применени для спектрофлуориметрического определения таллия все до области 0,01—0,08 мг/л. Изучено мешание 53 ионов при 100 кратном молярном избитке. Окисление с перекисью водорода до таллия (III) и экстракция из 1,5 *M* солляной кислоты в этиловый эфир с последовательным восстановлением с двуокисью серы отделяют микрограммовые количества таллия от всех мешающих катионов, кроме сурьми (V), висмута, золота и платины (IV). Значительные количества сульфата ($\times 10^6$) не мешают определению.

Thin-layer Chromatography—XV: Separation of terpene and sesquiterpene alcohols on silver nitrate-silica gel layers: E. STAHL and H. VOLLMANN, *Talanta*, 1965, **12**, 525. (Institut für Pharmakognosie der Universität des Saarlandes, 66 Saarbrücken, Bundesrepublik Deutschland.)

Summary—Mixtures of C_{10}-, C_{15}- and C_{20}- alcohols cannot be separated on normal silica-gel layers. A separation into groups with the same number of carbon atoms is possible on paraffin-impregnated layers. With gradient thin-layer chromatography it has been established that with increasing silver nitrate impregnation of silica gel, the separation of such mixtures is possible. The optimum and economic silver nitrate content is 3%. As solvent is used a mixture of methylene chloride-chloroform-ethyl acetate-n-propanol (50 + 50 + 5 + 5 v/v). The separation may be improved by multiple development.

Applications of nuclear and electron magnetic resonance in analytical chemistry: B. D. FLOCKHART and R. C. PINK, *Talanta*, 1965, **12**, 529. (Department of Chemistry, The Queens University, Belfast, N. Ireland.)

Summary—The principles of nuclear and electron magnetic resonance are briefly described, with reference to the use of these techniques in analytical chemistry. A wide field of analytical applications is reviewed in order that the scope and limitations of the methods may become apparent.

A thermogravimetric pyrolysis study of the interaction of di(1,2,3 benzotriazolatium)hexacyanoruthenate(IV) with certain organic amines: RAY F. WILSON and PHILIP MERCHANT, JR., *Talanta*, 1965, **12**, 559. (Department of Chemistry, Division of Natural and Physical Sciences, Texas Southern University, Houston, Texas, U.S.A.)

Summary—The thermogravimetric pyrolysis of the interaction products of certain organic amines and tetramethylammonium chloride with di(1,2,3-benzotriazolatium)hexacyanoruthenate(IV) is reported in this study.

ТОНКОСЛОЙНАЯ ХРОМАТОГРАФИЯ—XV: ВЫДЕЛЕНИЕ ТЕРПЕНОВ И СЕСКВИТЕРПЕНОВЫХ СПИРТОВ НА СЛОЯХ СИЛИКАГЕЛА ПРОПЫТАННЫХ НИТРАТОМ СЕРЕБРА:

E. Stahl and H. Vollmann, *Talanta*, 1965, **12**, 525.

Резюме—На обыкновенных слоях силикагела не удается разделять смеси C_{10}-, C_{15}- и C_{20}-спиртов. Между тем разделение по группам с одинаковым числом атомов углерода можно на слоях пропытанных параффином. При тонкослойной хроматографии на градиенте обнаружено что с растущим пропынием силикагела с нитратом серебра удается разделять такие смеси. Оптимальная концентрация нитрата серебра 3%. В качестве растворителя применяют смесь хлористый метилен—хлороформ—этилацетат—пропиловый спирт (50 + 50 + 5 + 5 по объему). Разделение можно улучшить повторенным хроматографированнием.

ПРИМЕНЕНИЕ ЯДЕРНОГО И ЭЛЕКТРОННОГО МАГНИТНОГО РЕЗОНАНСОВ В АНАЛИТИЧЕСКОЙ ХИМИИ:

B. D. Flockhart and R. C. Pink, *Talanta*, 1965, **12**, 529.

Резюме—Кратко описаны принципы методов ядерного и электронного магнитного резонансов ссиляясь на применение этих методов в аналитической химии. Рассматривается широкое поле аналитических применений с целю указать на возможности применения и недостатки этих методов.

ВЗАИМОДЕЙСТВИЕ ДИ(1,2,3-БЕНЗОТРИАЗОЛАТИУМ) ГЕКСАЦИАНОРУТЕНАТА(IV) С ИЗВЕСТНЫМИ ОРГАНИЧЕСКИМИ АМИНАМИ:

Ray F. Wilson and Philip Merchant Jr., *Talanta*, 1965, **12**, 559.

Резюме—В работе приведен термогравиметрический пиролиз продуктов взаимодействия известных органических аминов и хлорида тетраметиламмония с ди(1,2,3-бензотриазолатиум)-гексацианоруетенатом(IV).

Coprecipitation of iron(III) and zinc ions with aluminium tris-(8-hydroxyquinolate): T. H. Bailey and S. J. Lyle, *Talanta*, 1965, **12,** 563. (Londonderry Laboratory for Radiochemistry, University of Durham, Durham City, England).

Summary—Coprecipitation of tracer quantities of iron(III) and zinc with aluminium precipitated as the 8-hydroxyquinolate by isothermal evaporation of aqueous acetone solutions has been examined radiochemically. Iron(III) coprecipitation follows the logarithmic distribution law with $\lambda = 1{\cdot}47 \pm 0{\cdot}07$ for a wide range of acetate concentrations. Zinc shows similarities to yttrium and other rare-earth ions in only coprecipitating to a small extent, except on complete precipitation of the carrier. Results obtained from different media show small but distinguishable differences, particularly with increasing fractional precipitation of the carrier.

СООСАЖДЕНИЕ ИОНОВ ЖЕЛЕЗА (III) И ЦИНКА С ТРИС-(8-ОКСИХИНОЛИНАТОМ) АЛЮМИНИЯ:

T. H. BAILEY and S. J. LYLE, *Talanta*, 1965, 12, 563.

Резюме—Исследовано радиохимическим методом соосаждение индикаторных количесть железа(III) и цинка с алюминием в форме 8-оксихинолината путем изотермического выпаривания водно-ацетонового раствора. Соосаждение железа(III) соблюдается с логарифмическим законом распределения: $\lambda = 1{,}47 \pm 0{,}07$ для широкой области концентрации ацетата. Поведение цинка похоже иттрию и другими редкоземельными элементами—он соосаждается только в небольшой мере, кроме в случае полного осаждения носителя. Результаты получены в различных средах показывают небольшие но отличимые разницы, особенно с растущим дробным осаждением носителя.

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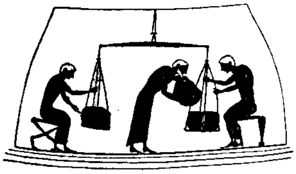

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[1] J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, **57**, 661.
[2] S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds*, Vol. 3. Pergamon Press, London, 2nd Ed., 1956, p. 214.
[3] A. B. Smith, *The Effect of Radiation on Strengths of Metals.* A.E.R.E., M/R 6329, 1962.
[4] W. Jones, *Brit. Pat.* 654321, 1959.

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REACTIONS OF METALLOCHROMIC INDICATORS ON MICELLES—I

GENERAL OBSERVATIONS*

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(*Received* 7 *July* 1964. *Accepted* 5 *January* 1965)

Summary—Purple-red alkaline solutions of Xylenol Orange are decolourised by the addition of cationic long-chain quaternary salts. A definite minimal ratio of the detergent to the indicator is necessary to bring about the full decolourising effect. The formation of micellar aggregates is supposed. In these one dye molecule is surrounded by at least five molecules of cetylpyridinium bromide and six molecules of cetyltrimethylammonium bromide, respectively. According to absorption spectra, the electronic structure of the Xylenol Orange in this state is that normally found at pH 6.4. Xylenol Orange, bounded in these aggregates, is capable of forming coloured complexes with a number of cations over a wider pH range than usual. Some ions, such as calcium and magnesium, not usually determined complexometrically with Xylenol Orange as an indicator may be successfully titrated using the modified indicator.

IT has been known for more than forty years that acid-base indicators have altered their colour in the presence of micelle-forming detergents.[1,2] This phenomenon, which takes place near the critical micelle concentration, has been explained by the preferential adsorption of one dissociation form of the indicator onto the detergent micelles, with the consequent displacement of the acid-base equilibrium in favour of this form.[3] Studying the effects of anionic, cationic and non-ionic detergents on a large number of dyes, Hartley[3] has found that the greatest colour change occurs when the charge on the detergent micelles is opposite to that of the indicator ions. In agreement with this "sign rule", the most marked effect has been observed for the interaction between an indicator with several charge points and an oppositely charged micelle.[4] However, for simple acid-base indicators, which exist in the appropriate pH-ranges at most as bi- or tervalent ions, the largest effect alters the apparent pKa by about 1·5 units. Metallochromic indicators of the complexan-type are in aqueous solutions present, depending on the pH, as anions whose charge may vary from one to six.[5,6] Because of the relatively high charge within certain pH-ranges, an extremely large colour effect could be expected from the interaction of these dyes and cation-active detergents.[4] Preliminary experiments, carried out with Xylenol Orange and cetylpyridinium bromide (CPB) and cetyltrimethylammonium bromide (CTAB), respectively, have confirmed this assumption. The addition of relatively small amounts of the above mentioned quaternary salts to the deeply coloured solutions of Xylenol Orange at pH 10–11 causes a marked colour change corresponding to a shift in pH of about 4 units towards the acid region. The addition of some cations

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* Presented in part before the Section of Analytical Chemistry at the XXth Meeting of the Czechoslovak Chemical Society, Žilina, July, 1963.

to this "decolourised" solution of Xylenol Orange results in the formation of intensely coloured (bright red to pure blue) complexes. Other complexan-type indicators behave in a similar manner.

This paper presents a more detailed study, undertaken in order to establish some general conditions of this phenomenon and to assess the analytical worth of the reaction. Xylenol Orange has been used as a model indicator.

EXPERIMENTAL

Reagents

All chemicals used throughout this work were of reagent grade purity.

Xylenol Orange. A $10^{-3}M$ standard solution was prepared by dissolving the calculated amount of the indicator (Lachema, Czechoslovakia) in redistilled water. This solution was prepared daily because of its low stability.[7] The working solutions were prepared by appropriate dilution of this stock solution.

Cetylpyridinium bromide and cetyltrimethylammonium bromide. Commercial products (Lachema) were used in the form of a $0{\cdot}01M$ solution in 20% methanol (v/v). The solutions were standardised by argentometric determination of the bromide ion content.

Buffer solutions. Ammonia-ammonium chloride buffer of pH 10·5 and a series of Sörensen's buffer solutions were used.

$0{\cdot}05M$ EDTA and $0{\cdot}01M$ metal solutions were prepared in the usual manner from appropriate salts.

Apparatus

Spectrophotometer. All absorbance measurements were made with either a spectrophotometer SF-4 (U.S.S.R.) using matched silica cells of 10-mm light-path, or a Pulfrich photometer (C. Zeiss, Jena, DDR) with 5-mm cells.

pH *meter.* pH values were determined with a glass electrode and a pH-meter Acidimetr AK (Kovodružstvo, Prague, Czechoslovakia).

RESULTS

Absorption spectra

The absorption spectra of the alkaline Xylenol Orange solutions show a characteristic absorption maximum at 580 mμ. After the addition of CPB (or CTAB), this maximum decreases, whilst a second absorption peak appears at 440 mμ. Visually, this change represents a discolouration of the original purple-red solution to pale greyish-pink, or in more dilute solutions to almost colourless.

Fig. 1 shows the absorption spectra of a solution of Xylenol Orange at pH 10·5 and on the same solution in the presence of CPB; to both solutions 2 drops of a $0{\cdot}05M$ EDTA solution have been added in order to avoid interference from any cations. Except for a small bathochromic shift of the absorption band at 580 mμ, the second curve agrees well with the dissociation form of Xylenol Orange at pH 6·4.[6]

The change of the absorption spectrum of Xylenol Orange occurs gradually, depending on the amount of quaternary salt added. In Fig. 2, the absorbance of Xylenol Orange at 580 mμ is plotted against the concentration of CPB and CTAB, respectively. All the curves obtained have three sections; the first, short horizontal section is caused by the influence of mineral salts added in the form of buffer solution; the second, descending section, represents the successive effect of the detergent on the indicator up to the point at which the additional increase of the quaternary salt concentration does not further diminish the absorbance of the dye.

It may be inferred from these curves that this point and hence the full decolourising effect is reached at the minimal ratio of the detergent to Xylenol Orange of 4·94 in the case of CPB and 5·96 for CTAB. When this ratio has been exceeded, the absorbance of Xylenol Orange remains unaltered even when an excess of several orders of magnitude of quaternary salts has been added.

It may also be noted that short-chain quaternary salts, such as tetramethylammonium bromide, do not affect the absorption spectra of Xylenol Orange.

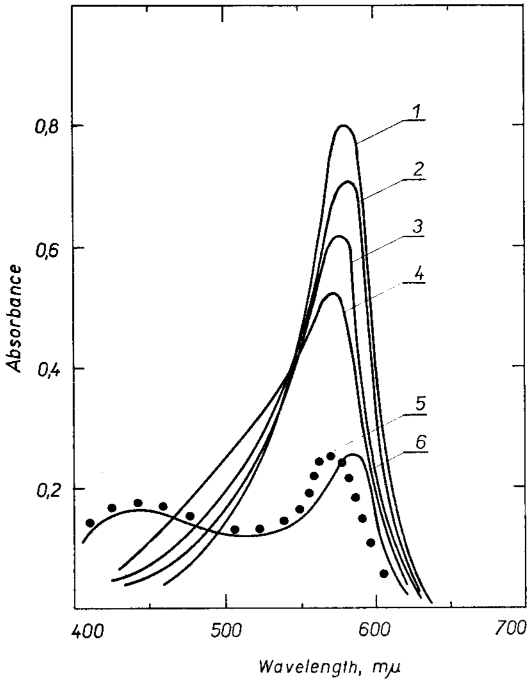

Fig. 1.—Absorption spectra of Xylenol Orange:—2·0 × $10^{-5}M$ XO at pH 10·5 (3); at pH 6·4 (5); at pH 10·5 with 5·0 × $10^{-4}M$ CPB (6); and excess of Ca (1); Zn (2) and Mn (4).

Effect of mineral salts

The presence of higher amounts of mineral salts disturbs the effect of the cationic detergents on the absorption spectra of Xylenol Orange. This negative influence may be seen in Fig. 2 where the length of the first horizontal branches of the curves is proportional to the amount of buffer solution added. Quantitatively, this effect is shown in Fig. 3, where the absorbance of the "decoloured" indicator solutions is plotted against the concentration of alkaline nitrates, chlorides and ammonium sulphate. The rate of increase in the absorbance caused by these salts depends mainly on the nature of the inorganic anion, the most marked one being brought about by the addition of nitrates. The individual cations, sodium, potassium and ammonium ion, have less effect on the absorption spectra of the dye. In the case of nitrates, the differences in the action of particular cations are virtually negligible. However, on addition of larger amounts of nitrates, a salting-out effect has been noticed; with the alkaline nitrates, whose concentrations exceed 0·2*M*, a reddish flocculant precipitate has been separated.

All these effects could be observed in the presence of long-chain quaternary

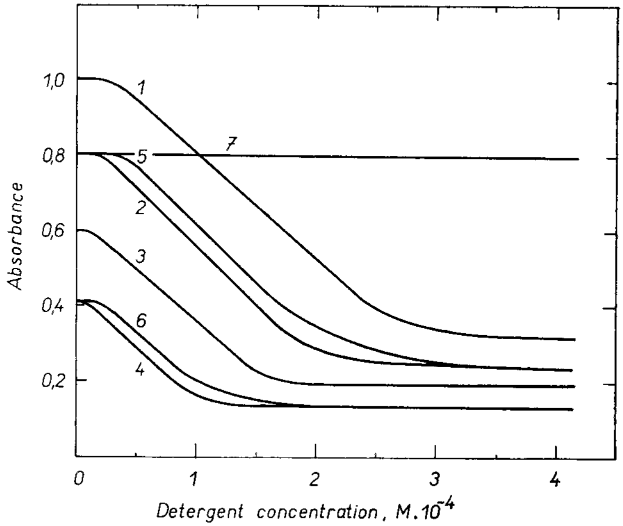

FIG. 2.—Effect of detergents absorbance of XO solutions at 580 mμ in the presence of CPB:—conc. XO = $5\cdot4 \times 10^{-5}M$ (1); $4\cdot1 \times 10^{-5}M$ (2); $3\cdot0 \times 10^{-5}M$ (3) and $2\cdot1 \times 10^{-5}M$ (4); in the presence of CTAB:—conc. XO = $4\cdot1 \times 10^{-5}M$ (5); $2\cdot1 \times 10^{-5}M$ (6); $4\cdot1 \times 10^{-5}M$ XO with tetramethylammonium bromide (7); pH of all solutions 10·5.

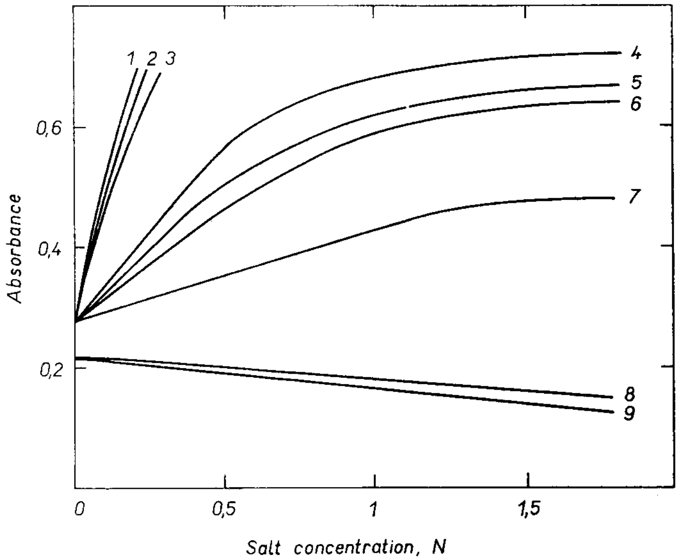

FIG. 3.—Effect of mineral salts—absorbance of XO at pH 10·5, 580 mμ, conc. of XO $4\cdot1 \times 10^{-5}M$ with $5 \times 10^{-4}M$ CPB:—Effect of NH_4NO_3 (1); $NaNO_3$ (2); KNO_3 (3); NH_4Cl (4); NaCl (5); KCl (6); $(NH_4)_2SO_4$ (7); $4\cdot1 \times 10^{-5}M$ XO at pH 6·4 without CPB, with NH_4NO_3 (8) and NH_4Cl (9).

salts only. Xylenol Orange, when alone at pH 6·4, shows at high concentrations of ammonium nitrate and ammonium chloride, only a slight decrease in absorbance associated with the normal "salt error" of acid-base indicator.

Complex formation

Xylenol Orange decolourised by the cationic detergent forms, in an alkaline medium, with numerous metal cations deep-coloured, water-soluble complexes. From the analytical viewpoint, the complexes of Ca(II), Ba(II), Sr(II), Mg(II), Cd(II), Zn(II), Ni(II), Co(II), Mn(II) and La(III) are the most interesting. The colours of most of these complexes range from bright red to bluish violet, whilst the complex of tervalent lanthanum is pure blue. Absorption spectra of the complexes with Ca(II), Zn(II) and Mn(II) are shown in Fig. 1.

The addition of EDTA to the solutions of these complexes brings about a decolouration to the original pale-pink colour. This colour change is instantaneous and sharp with the complexes of Ca(II), Ba(II), Mg(II), Cu(II), Cd(II), Zn(II) and Mn(II), but the complexes of Sr(II), Ni(II), Co(II), La(III) and other cations react slowly.

These complexes do not diffuse through a cellophane membrane into another detergent solution, whereas Xylenol Orange and its complexes in the absence of cationic detergents do.

Effect of temperature

No change in the absorbance of Xylenol Orange solutions in the presence of detergent could be observed in the temperature range from 20° to 60°.

DISCUSSION

All our attempts to isolate a product from the interaction of Xylenol Orange and detergent failed; the product is very soluble in water, and from the concentrated solutions, a mixture of detergent crystals and amorphous dye particles was always isolated. This mixture gave the individual components when washed out with an appropriate solvent. These results indicate that the interaction product exists in aqueous solutions as micellar aggregates.

The fact that the formation of micellar aggregates occurs at lower detergent concentrations than the critical micelle concentration (estimated in pure solutions by various methods) does not disagree with this supposition. It is well known that in the presence of an appropriate dye, the induced micelle formation occurs even with concentrations at which the detergent alone does not form micelles.[8]

From the experiments carried out it is not evident which of the groups of the indicator are involved in the bond with the detergent. However, the change in absorption spectra of Xylenol Orange, on addition of the detergent, suggests that the bond must involve the phenolic group.[9] Further, because the absorption spectra of the aggregates and that of free Xylenol Orange at pH 6·4 are identical, a similar resonance structure of the indicator may be assumed in both instances. The metal ion is able to react with the indicator which, however, still remains involved in the micellar aggregates, as evidenced by its inability to pass through cellophane membranes.

High concentrations of mineral salts prevent the formation of dye-detergent micelles. This is probably caused by the inorganic anion displacing the dye as a counter-ion.

Although the theory is incomplete, the practical consequences in analytical chemistry are of some interest. The complexan-type metallochromic indicators of the sulphonphthalein series, which are superior because of their excellent colour properties, have had no previous application in an alkaline medium. The use of a suitable cationic detergent enables these indicators to be used over practically the whole pH range. This fact may be exploited in the field of complexometric titrations as well as in the spectrophotometric analysis of some metal cations. Both these possibilities are the subject of further detailed studies.

Acknowledgment—The authors wish to express their thanks to Mr. J. Körbl (Biochemical and Pharmaceutical Research Institute, Prague, Czechoslovakia) for his helpful discussion of this work.

Zusammenfassung—Purpurrot gefärbte alkalische Lösungen von Xylenolorange werden durch den Zusatz von kationaktiven langkettigen quaternären Salzen entfärbt. Ein bastimmtes Grenzverhältnis des oberflächenaktiven Mittels zum Indikator ist erforderlich um den Entfärbungseffekt voll zur Geltung zu bringen. Es wird die Bildung von mizellenartigen Aggregaten vorausgesetzt. In diesen Aggregaten ist jedes Farbstoffmolekül mit mindestens fünf Molekülen Cetylpyridiniumbromid, beziehungsweise mit sechs Molekülen Cetyltrimethylammoniumbromid umgeben. Absorptionsspektren zeigen, dass die Elektronenstruktur von Xylenolorange in diesem Zustand der üblichen, bei pH 6,4 vorgefundenen Struktur entspricht. Xylenolorange in der Form solcher Aggregate besitzt die Fähigkeit gefärbte Komplexe mit gewissen Kationen in einem breiteren pH-Bereich zu bilden als in der normalen Form. Einige Ionen, wie zum Beispiel Kalzium und Magnesium, welche gewöhnlich nicht mit Xylenolorange als Indikator bestimmt werden, können, erfolgreich mit Hilfe des modifizierten Indikators titriert werden.

Résumé—Les solutions alcalines rouge-pourpre de Xylénol Orangé sont décolorées par l'addition de sels quaternaires cationiques à longue chaîne. Un rapport minimal défini entre le détergent et l'indicateur est nécessaire pour apporter l'effet décolorant total. On suppose la formation d'agrégats micellaires. Dans ces agrégats, une molécule de colorant est entourée par au moins cinq molécules de bromure de cétylpyridinium et six molécules de bromure de cétyltriméthylammonium, respectivement. Selon les spectres d'absorption, la structure électronique du Xylénol Orange dans cet état est celle que l'on trouve normalement à pH 6,4. Le Xylénol Orangé, lié dans ces agrégats, est capable de former des complexes colorés avec un certain nombre de cations dans un domaine de pH plus grand que d'ordinaire. Quelques ions, comme le calcium et le magnésium, que l'on ne dose pas habituellement avec le Xylénol Orangé comme indicateur, peuvent être dosés avec succès en employant l'indicateur modifié.

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REACTIONS OF METALLOCHROMIC INDICATORS ON MICELLES—II†

APPLICATION OF XYLENOL ORANGE TO CHELATOMETRIC TITRATIONS IN AN ALKALINE MEDIUM*

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(*Received* 7 *July* 1964. *Accepted* 5 *January* 1965)

Summary—Xylenol Orange in the presence of cetylpyridinium bromide has been applied as a metallochromic indicator for the complexometric determination of some metal cations in an alkaline medium. Precise successive determinations of some pairs of metals in the same solution are possible.

IN the introductory communication of this series,[1] the behaviour of alkaline Xylenol Orange solutions in the presence of micelle-forming cationic detergents has been described. From the analytical point of view, the most interesting property of the aggregates formed is their ability to form coloured complexes with various cations. Some of them react practically instantaneously with EDTA solution, so that their successful application in complexometric titrations could be expected. In preliminary experiments, among the metals forming sufficiently stable complexes with EDTA in the alkaline region, the most promising results have been obtained in the titration of calcium(II), magnesium(II), cadmium(II), zinc(II) and manganese(II). The extension of the working range of Xylenol Orange to alkaline solutions allows the successive determination of some pairs of metals in the same solution. The results of such determinations are presented in this paper.

EXPERIMENTAL

Reagents

EDTA. 0·025 and 0·05*M* solutions were prepared from disodium ethylenediaminetetra-acetate (Chelaton 3, Lachema, Czechoslovakia) and standardised in the usual manner.

Metal ions. 0·025*M* solutions of calcium, magnesium, cadmium, zinc lead and manganese were prepared from appropriate salts and standardised by means of conventional EDTA titrations.

Buffers. Ammoniacal buffer solution of pH 10·5 and solid hexamethylenetetramine were used for pH adjustment.

Indicator. Xylenol Orange was used as a 1:100 solid mixture finely ground with potassium chloride.

Cetylpyridinium bromide. Used in the form of a saturated solution in 20% aqueous methanol.

Nitric acid. 10% Aqueous solution.

All chemicals used in this work were of reagent-grade purity.

Procedure

Determination of single metal ions. Dilute the sample solution to 100 ml, and add 10 ml of pH 10·5 buffer solution followed by 1 ml of detergent solution and Xylenol Orange mixture. Titrate with EDTA to the end-point colour change.

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† Part I: see reference 1.

* Presented in part before the Section of Analytical Chemistry at the XXth Meeting of the Czechoslovak Chemical Society, Žilina, July, 1963.

Determination of pairs of metal ions. The metal ion pairs are selected so that one ion may be titrated in acid and the other in alkaline solution. Acidify the solution to be titrated with a few drops of nitric acid, then add the indicator and solid hexamethylenetetramine. Titrate with EDTA till the solution changes from dark red to clear lemon-yellow.[2,3] Adjust the pH to 10·5 with 10 ml of ammoniacal buffer solution, add 1–2 ml of detergent solution and titrate the second cation with EDTA.

RESULTS

Determination of single metal ions

The results of the determination of individual cations in an alkaline medium are given in Table I. All the tabulated values are the means of ten determinations.

TABLE I.—TITRATION OF INDIVIDUAL CATIONS

Ion	Taken, *mg*	Found, *mg*	Standard deviation, *mg*
Ca^{2+}	5·06[a]	5·06	±0·011
	10·11[a]	10·11	±0·010
	20·33[b]	20·32	±0·017
Zn^{2+}	5·62[a]	5·62	±0·014
	11·24[a]	11·23	±0·016
	33·10[b]	33·09	±0·028
Mn^{2+}	5·84[a]	5·86	±0·007
	11·71[a]	11·71	±0·010
	28·25[b]	28·25	±0·029
Mg^{2+}	6·14[b]	6·14	±0·006
	12·28[b]	12·28	±0·007
Cd^{2+}	12·71[b]	12·69	±0·042
	31·78[b]	31·80	±0·053

[a] 0·025*M* EDTA used.
[b] 0·05*M* EDTA used.

The average recoveries of the determined cations agree well with the amounts taken. The standard deviations, show, especially in the case of determinations of calcium, magnesium and manganese, the excellent reproducibility of individual results. The results obtained for cadmium(II) are less satisfactory; nevertheless, even in this case the results compare favourably with those from previously published methods.

In all the determinations, the end-point colour change was distinct and sharp, within 1-2 drops of the titrant solution. The colours of the indicator-metal complexes vary with the metal ion; those of magnesium and zinc are red; that of manganese is violet; and those of calcium and cadmium are blue-violet. At the equivalence-point these colours change to colourless or pale grey, depending upon the amount of the indicator added. With calcium and cadmium, the colour change passes through a sky-blue shade close to the equivalence-point, which makes the colour change more remarkable.

Determination of pairs of metals

The presence of a metal of the alkaline earth metal group does not interfere with the first determination in acid solution, and the accuracy is unimpaired.

As described in the preceding paper,[1] mineral salts affect the formation of the indicator-detergent complex. Therefore, in these determinations, after the adjustment of pH, a greater amount of the detergent solution is necessary in order to obtain satisfactory results.

In all the titrations of the second cation in the alkaline region, the end-point colour change of the indicator is much better than that obtained when the corresponding metal ions are alone. This phenomenon is probably explained by the following reaction taking place, at least to some extent,

$$\text{Pb-EDTA} + \text{Ca-In} \rightleftharpoons \text{Pb-In} + \text{Ca-EDTA}$$

so that at the end-point the lead-indicator complex is being titrated with consequent improvement in colour change.

TABLE II.—TITRATION OF PAIRS OF METALS

Taken, *mg*		Found, *mg*		95% Confidence interval, *mg*	
Zn	Mg	Zn	Mg	Zn	Mg
3·31	10·99	3·31	10·98	±0·016	±0·012
9·92	8·55	9·87	8·54	±0·033	±0·012
16·53	6·11	16·54	6·11	±0·033	±0·012
23·15	3·66	23·16	3·66	±0·016	±0·012
29·76	1·22	29·78	1·23	±0·033	±0·012
Pb	Ca	Pb	Ca	Pb	Ca
10·58	18·13	10·51	18·13	±0·055	±0·041
31·55	14·10	31·57	14·11	±0·053	±0·021
52·58	10·07	52·56	10·07	±0·105	±0·020
73·61	6·04	73·60	6·05	±0·053	±0·020
94·64	2·01	94·63	2·02	±0·160	±0·020

Table II shows the results of titrations of the metal pairs zinc-magnesium and lead-calcium. The titrations were performed for various ratios of cations. The values given in the table are averages of five determinations. The Dean-Dixon method,[6] which has been recommended for the statistical evaluation of data based on a small number of observations, was used. As may be seen from the tabulated values of confidence intervals, the results of individual titrations of the second cation have good precision.

DISCUSSION

Among the large number of metallochromic indicators used in complexometric titrations, Xylenol Orange is outstanding. However, its application has been limited by its own acid-base indicator properties, to the acid region. The interaction of Xylenol Orange with cation-active detergents permits the extension of its useful range to pH 11, where it behaves like its "acid" form, giving with many cations "normal" complexes (*cf.*[4,5]).

The titrations described in this communication represent only a few examples of the cases in which Xylenol Orange can be used in the presence of cationic detergents. For most of these determinations, of course, other, more or less suitable indicators have been proposed todate. Nevertheless, because of the excellent colour properties of Xylenol Orange which are retained even in these instances, one can suppose that these new possibilities will find a very wide practical application in complexometric analysis.

Zusammenfassung—Xylenolorange wurde als Metallfarbindikator in Gegenwart von Cetylpyridiniumbromid zur komplexometrischen Bestimmung einiger Kationen in alkalischer Lösung angewendet. Es ist möglich gewisse Metallpaare in derselben Lösung aufeinander folgend sehr genau zu bestimmen.

Résumé—Le Xylénol Orangé en présence de bromure de cétylpyridinium a été appliqué, en tant qu'indicateur métallochrome, au dosage complexométrique de quelques cations dans un milieu alcalin. Il est possible d'effectuer les dosages successifs précis de quelques paires de métaux dans la même solution.

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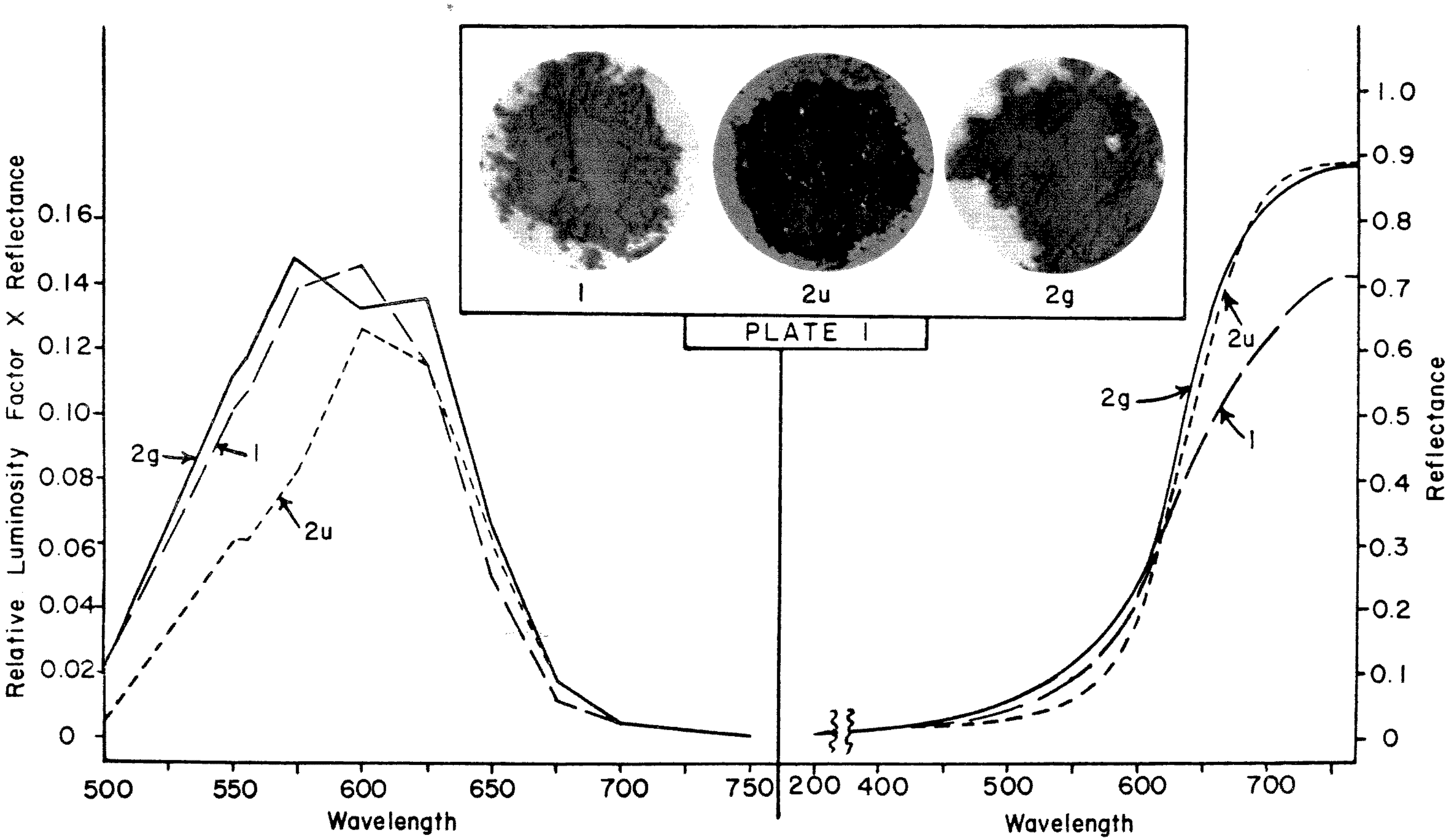

1a 1b

FIG. 1—Reflectance spectra of the solvated uranium 8-hydroxyquinolates:
1 —$(UO_2Q_2)_2 \cdot HQ$, orange;
2u—$UO_2Q_2 \cdot HQ$, dark red, unground;
2g—$UO_2Q_2 \cdot HQ$, orange, ground.

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REFLECTANCE SPECTRA OF TWO SOLVATED URANIUM 8-HYDROXYQUINOLATES

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Summary—On precipitation of uranyl 8-hydroxyquinolate from homogeneous solution, two different chelates are obtained.

$UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$

is dark red whereas $[UO_2(C_9H_6NO)_2]_2 \cdot C_9H_6NOH$ is orange. On grinding, the dark-red chelate becomes orange. Reflectance spectra are used to explain the initial colour difference as well as the change in colour of the dark-red compound to orange on grinding.

IN 1961 Bordner *et al.*[1] precipitated two uranium 8-hydroxyquinolates from homogeneous solution with 8-hydroxyquinoline (HQ) generated by hydrolysis of 8-acetoxyquinoline. Table I summarises the properties of the two precipitates. When the dark-red compound, $UO_2Q_2 \cdot HQ$, is ground, it assumes an orange colour very similar to that of $(UO_2Q_2)_2 \cdot HQ$. To explain the colour differences and colour change on grinding the compound $UO_2Q_2 \cdot HQ$, a study of the reflectance spectra of the different compounds was undertaken.

TABLE I.—PROPERTIES OF THE URANIUM 8-HYDROXYQUINOLATES PRECIPITATED FROM HOMOGENEOUS SOLUTION

Formula	$UO_2Q_2 \cdot HQ$	$(UO_2Q_2)_2 \cdot HQ$
Colour of precipitate	dark red	orange
pH of precipitation	5·0	6·8
Excess of reagent used in precipitation procedure	*ca.* 20-fold[1]	2-fold[1]

Reflectance and eye response spectra

The reflectance spectra of the various compounds were obtained with a Cary 14 Spectrophotometer and are shown in Fig. 1b. In general appearance the spectra are very similar. All exhibit high reflectance in the red region around 750 mμ. Sample 1 (orange) has a smaller reflectance in this region whereas the reflectances of sample 2u (dark red) and sample 2g (orange), which are chemically identical, are larger and close to each other. Between 500–600 mμ, or the yellow-orange region of the spectrum, a decrease in reflectance is observed in the order 2g > 1 > 2u. At the ultraviolet end of the spectrum all three show very small but identical reflectance.

To explain these colour phenomena, it is first necessary to consider eye sensitivity. As a measuring instrument for luminosity, the eye is very selective in that it does not respond equally to radiations of different wavelengths. In the region 500–600 mμ, where colours range from green to yellow-orange, the eye is very sensitive, but in the

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region around 750 mμ (red) it is remarkably insensitive. A measure of eye sensitivity at normal brilliance levels for radiation of different wavelengths is given by the *Relative Luminosity Factor* (Eye Response). A part of the values for this factor given by the I.E.S. Nomenclature and Photometric Standards, American Standards Association, ASA C-42, 1941, is reproduced in Table II. The eye exhibits its maximum response at a wavelength of 555 mμ and the values for other wavelengths are given relative to this.

Because of the insensitivity of the eye in the red region around 750 mμ, it requires a large difference in reflectance for the eye to observe the difference. Further, in the region 500–600 mμ, where peak eye sensitivity occurs, small differences in reflectance will have a considerable effect on the eye. Thus, samples 1 and 2g, despite high reflectance around 750 mμ as shown in Fig. 1b, appear predominantly orange to the eye because of moderate reflectance in the eye-sensitive region, whereas sample 2u, which has a reflectance as great as 2g in the red, appears red because its contribution to the reflectance in the eye-sensitive region is much less in comparison to samples 1 and 2g.

TABLE II.—RELATIVE LUMINOSITY FACTOR
(Eye Response)

Wavelength of radiation, *mμ*	Factor
500	0·323
510	0·503
520	0·710
530	0·862
540	0·954
550	0·995
555	1·000
560	0·995
570	0·952
580	0·870
590	0·757
600	0·631
.	.
.	.
.	.
700	0·0041
710	0·0021
720	0·00105
730	0·00052
740	0·00025
750	0·00012
760	0·00006

The significance of the colour phenomena becomes more apparent by converting the reflectance-spectra values obtained with the spectrophotometer to *eye-response* spectra, which corresponds to what the eye actually sees. This is done by plotting the product of the relative luminosity factor and the reflectance at a particular wavelength *versus* the wavelength. The results are shown in Fig. 1a.

From the graphs it will be seen that sample 2g shows its highest reflectance at 575 mμ (orange) with a smaller contribution at 625 mμ (red-orange). To the eye, therefore, this substance will appear predominantly orange but with a reddish tinge to it. Sample 1 will appear orange in colour. Sample 2u, on the other hand, with its major peak at 600–625 mμ appears quite red because its reflectance in the yellow-orange region is much lower than for the other two samples.

The reddish tinge in sample 2g can be seen in Plate 1 of Fig. 1, where 1 is the orange precipitate obtained at pH 6·8 [$UO_2Q_2)_2\cdot HQ$] and 2u the dark-red precipitate obtained at pH 5·0 ($UO_2Q_2\cdot HQ$). The small difference in colour between samples 1 and 2g could be related to a slight difference in structure.

The importance of the eye-response spectra becomes quite evident in that differences in the red region (750 mμ), which looked significant in Fig. 1b, now become insignificant to the eye and that small differences in the yellow-orange region (500–600 mμ) in Fig. 1b become significant.

Effect of particle size on reflectance

While the foregoing discussion gives an explanation for the colour of the precipitate as seen by the eye, it does not offer an explanation for the change in colour of dark-red sample 2u to orange on grinding. The particle size is the principal factor involved in this phenomenon.

Johnson[2] has shown that a strong increase in reflectance takes place when the particle size of a sample decreases. An electron microscopic examination of sample 2u (dark red) showed it to be comprised of particles very much larger than those in sample 1 (orange). Thus, when 2u is ground, there is an increase in reflectance in the eye-sensitive yellow-orange region around 525 mμ (*cf.* reflectance values for 2u and 2g in Fig. 1b). Hence, 2g looks more orange to the eye. However, there is no similar increase in reflectance around 750 mμ on grinding 2u, but this is in agreement with Johnson's[2] views that deductions about reflectance increases on grinding are not accurate where the reflectance values are greater than 0·8, as in the present case.

When samples 1 and 2g are ground to exactly the same particle size, their reflectance spectra curves are coincident in the yellow-orange region and differ only in the red region.

Effect of precipitation conditions on formation of uranium chelates

In the simpler uranyl compounds, *e.g.*, uranyl nitrate, the uranium atom is octa-co-ordinate. The central atom forms 6 bonds, partly covalent, which are in a plane orthogonal to the O—U—O plane. Thus, the uranyl group will show sexa-covalent character and involve the use of f-orbitals.[3] Evidence in favour of this assumption is based on the strong tendency of the uranyl group to co-ordinate molecules of water in the solid state and solution.[4] Sacconi *et al.*[5] have also shown that the uranyl group, even when bonded to two diketone radicals, tends to co-ordinate donor molecules. It would appear, therefore, that the uranyl group, even after reacting with two molecules of 8-hydroxyquinoline, is *co-ordinatively unsaturated* and capable of adding further molecules of solvation. In such circumstances, the rate of precipitation and the number of molecules of reagent available might determine the particular chelate formed.

As seen in Table I, the dark-red compound $UO_2Q_2\cdot HQ$ is precipitated at pH 5·0 with a calculated excess of reagent of about 20-fold present, whereas at pH 6·8 for the orange precipitate ($(UO_2Q_2)_2\cdot HQ$) there is a 2-fold excess of reagent present. For comparison, two precipitations were carried out with the amounts of reagent used reversed, *i.e.*, where formerly a 2-fold excess of reagent was employed, a 20-fold excess was now used and *vice versa*; all other conditions were maintained as before. The results were that, whereas previously at pH 6·8 an orange precipitate had been obtained, a dark-red precipitate now formed. The precipitate obtained at pH 5·0 was still red, although the amount of precipitate formed was quite small because of the higher acidity and the lack of precipitant. The results thus confirm that the number of available molecules of reagent has a determining influence on the particular uranium chelate formed.

Acknowledgment—The authors acknowledge the partial assistance of the United States Atomic Energy Commission in supporting the investigation described herein under Contract AT(11-1)-582. Thanks are also due to Dr. K. Takiyama who examined the precipitates by electron microscopy.

Zusammenfassung—Bei der Fällung von Uran-8-hydroxychinolat aus homogener Lösung erhält man zwei verschiedene Chelate.

$$UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$$

ist dunkelrot, $[UO_2(C_9H_6NO)_2]_2 \cdot C_9H_6NOH$ dagegen orange. Beim Mahlen wird das dunkelrote Chelat orange. Mit Hilfe von Reflexionsspektren wird der anfängliche Farbunterschied sowohl als auch die Farbänderung der dunkelroten Verbindung nach orange beim Mahlen erklärt.

Résumé—Lors de la précipitation du 8-hydroxyquinolinate d'uranyle en milieu homogène, on obtient deux chélates différents.

$$UO_2(C_9H_6NO)_2,C_9H_6NOH$$

est rouge foncé, cependant que $[UO_2(C_9H_6NO)_2]_2,C_9H_6NOH$ est orangé. Par broyage, le chélate rouge foncé devient orangé. On utilise les spectres de réflexion pour expliquer la différence de couleur initiale ainsi que le changement de couleur du composé rouge foncé en orangé lors du broyage.

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INFRARED SPECTRA OF CHELATE COMPOUNDS—IV†

A STUDY OF THE URANYL CHELATES OF 8-HYDROXYQUINOLINE IN THE REGION 5000–250 cm^{-1}

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Summary—Previous investigations have shown that two different uranium chelates of 8-hydroxyquinoline can be precipitated from homogeneous solution. Dark red $UO_2(C_9H_6NO)_2{\cdot}C_9H_6NOH$ is obtained at pH 5·0 and orange $[UO_2(C_9H_6NO)_2]_2{\cdot}C_9H_6NOH$ at pH 6·8; the *normal* chelate $UO_2(C_9H_6NO)_2$ is green. The infrared spectra of the solvated compounds have been examined in the range 5000–250 cm^{-1} and that of the normal chelate in the range 5000–650 cm^{-1}. From this it is concluded that the solvated chelates have very similar structures.

IN earlier parts of this series[1–3] the results of infrared investigations of bivalent and tervalent metal chelates of 8-hydroxyquinoline in the region 5000–250 cm^{-1} were reported. In the present work the uranium chelates have been studied.

In 1933 Frere[4] precipitated the uranium chelate of 8-hydroxyquinoline by conventional means and obtained a deep brick-red precipitate for which the formula $UO_2Q_2{\cdot}HQ$ (where $Q = C_9H_6NO$) was given. Since then it has been recognised that uranium forms two compounds with 8-hydroxyquinoline, a red compound with the above structure and the green *normal* chelate UO_2Q_2.[5] However, in 1961 Bordner *et al.*[6] precipitated two different uranium(VI) 8-hydroxyquinolates from homogeneous solution with 8-hydroxyquinoline generated by the hydrolysis of 8-acetoxyquinoline. One of the precipitates was dark red in colour while the other was orange. The analytical data indicated the composition of the two uranium chelates to be different. For the dark-red precipitate, obtained at pH 5·0, the formula $UO_2Q_2{\cdot}HQ$ fitted the data and for the orange chelate, precipitated at pH 6·8, $(UO_2Q_2)_2{\cdot}HQ$ was appropriate.

EXPERIMENTAL

Infrared measurements

The precipitates were obtained by the procedures referred to above. Both the potassium bromide disc technique and the Nujol-mull technique were used to obtain the infrared spectra. In the former the discs were prepared using a Perkin-Elmer die in conjunction with an Elmes hydraulic press capable of delivering 23,000 lb total load on a ram 3″ in diameter. Before use, spectroscopic-grade potassium bromide was dried at 150° for 24 hr and ground to pass 100 mesh.

All spectra were recorded on a Perkin-Elmer Model 21 Spectrophotometer with a caesium bromide prism. Polystyrene was used for calibration purposes.

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† Part III: reference 3.

RESULTS

The spectra obtained for the solvated metal chelates are shown in Figs. 1–4 (the spectrum for 8-hydroxyquinoline has been reported previously[1,2]). The principal absorption peaks (μ) in these spectra are as follows:

$UO_2(C_9H_6NO)_2{\cdot}C_9H_6NOH$ and $[UO_2(C_9H_6NO)_2]_2{\cdot}C_9H_6NOH$. 33·85, 28·5, 23·11, 20·55, 19·77, 18·29, 16·6, 16·01, 15·5, 13·68, 13·32, 13·0, 12·73, 12·54, 12·46, 12·3, 12·17,

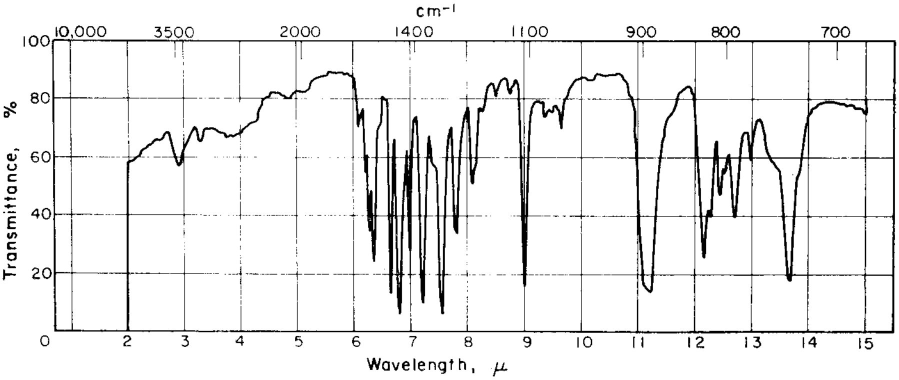

FIG. 1.—The infrared spectrum of $UO_2(C_9H_6NO)_2{\cdot}C_9H_6NOH$ obtained at pH 5·0 in the region 2–15 μ [1 mg of $UO_2(C_9H_6NO)_2{\cdot}C_9H_6NOH$ in 400 mg of KBr].

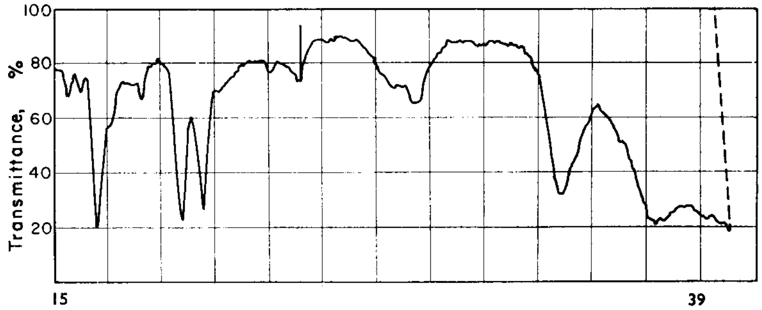

FIG. 2.—The infrared spectrum of $UO_2(C_9H_6NO)_2{\cdot}C_9H_6NOH$ obtained at pH 5·0 in the region 15–40 μ [2 mg of $UO_2(C_9H_6NO)_2{\cdot}C_9H_6NOH$ in 400 mg of KBr].

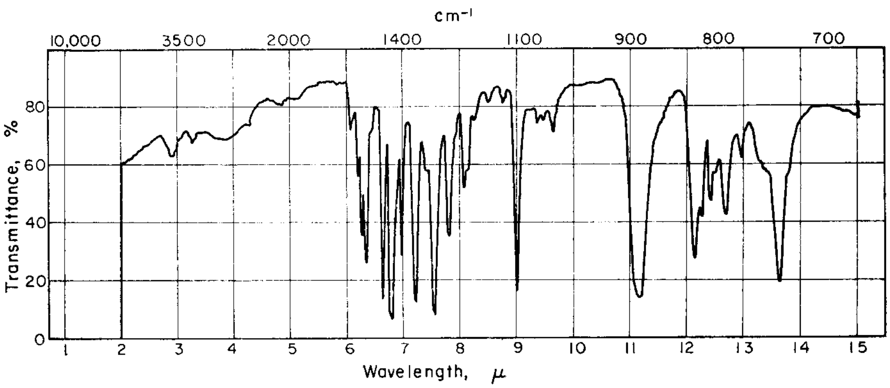

FIG. 3.—The infrared spectrum of $[UO_2(C_9H_6NO)_2]_2{\cdot}C_9H_6NOH$ obtained at pH 6·8 in the region 2–15 μ (1 mg of $[UO_2(C_9H_6NO)_2]_2{\cdot}C_9H_6NOH$ in 400 mg of KBr).

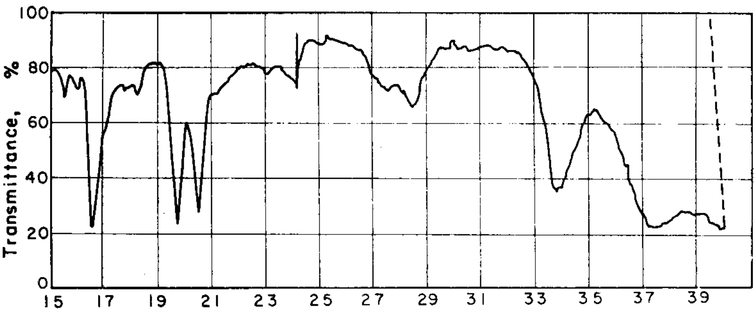

FIG. 4.—The infrared spectrum of $[UO_2(C_9H_6NO)_2]_2 \cdot C_9H_6NOH$ obtained at pH 6·8 in the region 15–40 μ (2 mg of $[UO_2(C_9H_6NO)_2]_2 \cdot C_9H_6NOH$ in 400 mg of KBr).

11·22, 9·66, 9·5, 9·37, 9·02, 8·78, 8·52, 8·3, 8·16, 8·1, 7·82, 7·56, 7·24, 7·0, 6·8, 6·66, 6·36, 6·28, 6·22, 6·09, 5·14, 4·87, 3·27, 2·92.

Only the principal peaks for the uranium chelate precipitated at pH 5·0 are given, because those for the precipitate obtained at pH 6·8 appeared to be identical. However, in the region between about 9 μ (1100 cm^{-1}) and 14 μ (700 cm^{-1}), it looked as if small differences in the spectra might exist. To investigate more closely if these tendencies were real or imaginary the spectra of the two metal chelates were obtained at improved resolution on the Beckman IR-7 instrument between 650 and 1100 cm^{-1}. The Nujol-mull technique was employed, the concentration of the chelate being adjusted until the best resolution was obtained. The spectrum of the dark-red precipitate obtained at pH 5·0 is shown in Fig. 5 and that of the orange precipitate obtained at pH 6·8 in Fig. 6.

Between the two spectra minor differences arise:

(1) A small peak always occurs at 678 cm^{-1} in the spectrum of the dark-red sample (Fig. 5) which is absent in that of the orange sample (Fig. 6).

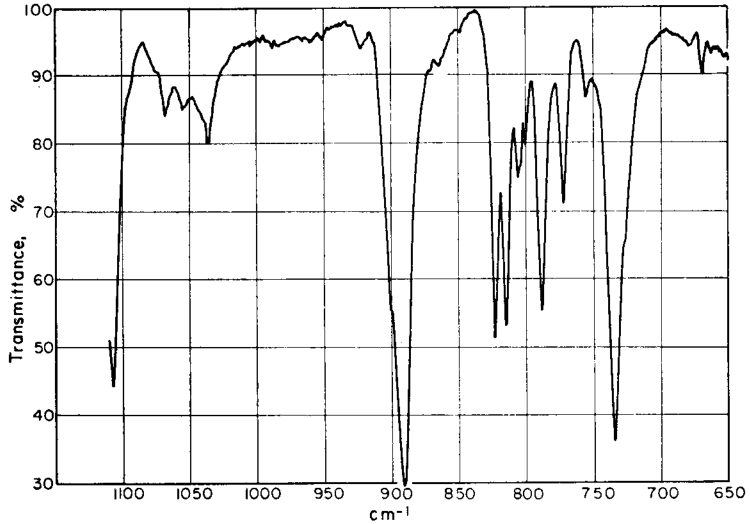

FIG. 5.—The infrared spectrum of $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$ obtained at pH 5·0 in the region 9–15·5 μ ($[UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$ in a Nujol mull].

(2) The lengths of the major peaks at 823 and 813 cm^{-1} are reversed in the spectra of the two chelates.

(3) In the major peak at 888 cm^{-1} a shoulder occurs in both spectra, but it was always more clearly resolved in that of the orange sample.

To investigate more closely the shoulders on the peak at 888 cm^{-1} as indicated in (3) above, a closer examination was carried out, at the greatest sensitivity available, in the spectral region 820–910 cm^{-1}. Little improvement was obtained except that, in the spectrum of the dark-red chelate, the major peak occurred at 891 cm^{-1} (888 cm^{-1} in the orange compounds) and the shoulder in the spectrum of the dark-red chelate appeared to be resolved more clearly.

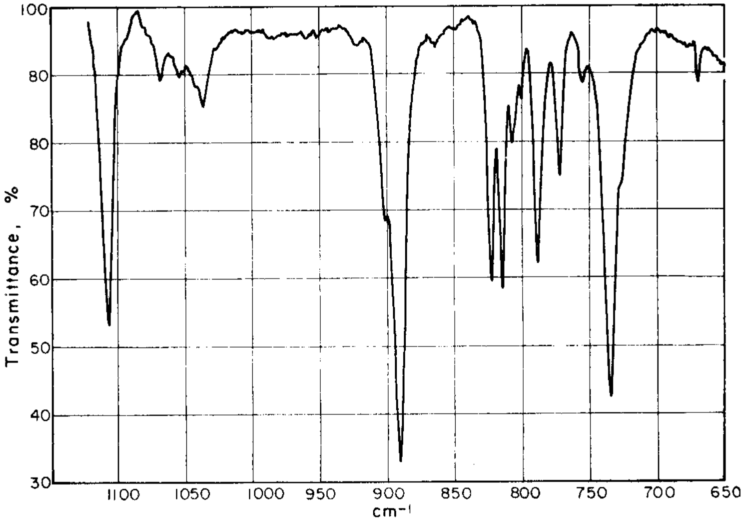

FIG. 6.—The infrared spectrum of $[UO_2(C_9H_6NO)_2]_2{\cdot}C_9H_6NOH$ obtained at pH 6·8 in the region 9–15·5 μ ($[UO_2(C_9H_6NO)_2]_2{\cdot}C_9H_6NOH$ in a Nujol mull).

$UO_2(C_9H_6NO)_2$. The unsolvated chelate, UO_2Q_2, is obtained by heating $UO_2Q_2{\cdot}$HQ at 210–215°.[7] The infrared spectrum is shown in Fig. 7. It will be seen that the spectrum differs in many respects from those of the dark-red chelate and the orange chelate (Figs. 5 and 6). If the three spectra are checked peak by peak it will be found that the differences between UO_2Q_2 and the other two are based principally on the disappearance or shifts of peaks from the latter. The principal differences are as follows:

(1) The peaks at 1056 and 1068 cm^{-1} occurring in the spectra of the dark-red and orange compounds have disappeared from the spectrum of UO_2Q_2.

(2) The peak around 890 cm^{-1} attributed to UO_2^{2+} stretching in the spectrum of the dark-red and orange compounds has shifted to 920 cm^{-1} in the spectrum of UO_2Q_2 and the shoulders on this peak which were so clearly indicated in the former have disappeared.

(3) In the spectra of the dark-red and the orange compounds two peaks occurred at 823 and 813 cm^{-1} and the lengths of the peaks differed clearly in the two spectra. In the case of the spectrum of UO_2Q_2 these peaks are shifted, occurring at 878

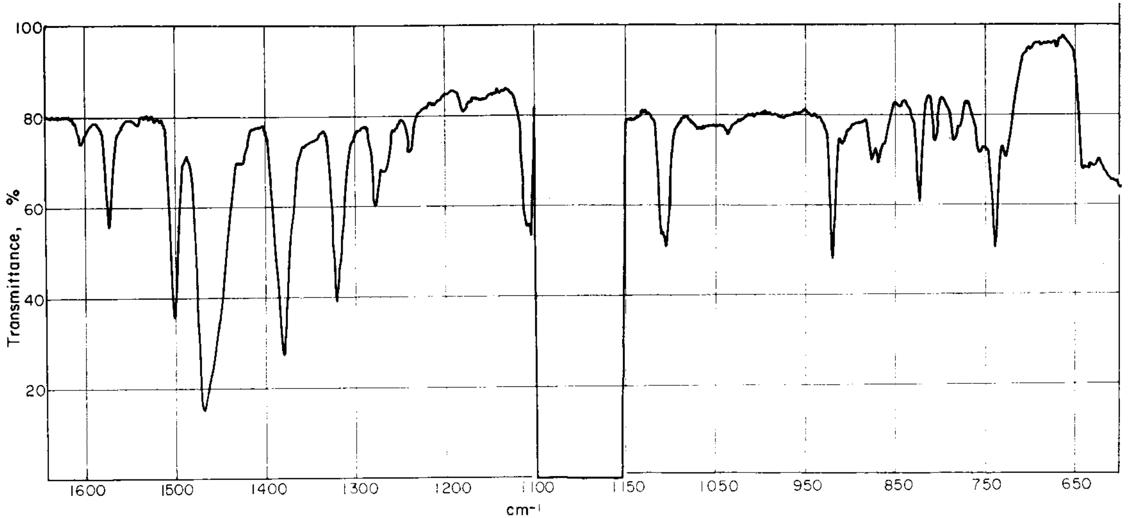

FIG. 7.—The infrared spectrum of the *normal* $UO_2(C_9H_6NO)_2$ in the region 6-15 μ [$UO_2(C_9H_6NO)_2$ in a Nujol mull].

and 869 cm^{-1}, respectively, and the lengths of the peaks again differ, being in the same order as for the orange compound.

CONCLUSION

The structure of the dark-red compound, $UO_2(C_9H_6NO)_2{\cdot}C_9H_6NOH$, has been discussed by several groups of authors,[5,8,9] but no mention is made by any of them of the orange chelate, $[UO_2(C_9H_6NO)_2]_2{\cdot}C_9H_6NOH$. In the present work it was hoped that the infrared investigation might reveal sufficient differences to allow a definite conclusion to be drawn about the structures of the two compounds. However, as the above results show, the spectral differences are small, so that the only conclusion possible is that the two chelates are structurally similar and that differences, if they do exist, are very small. This similarity of the two chelates has also been demonstrated by a study of their reflectance spectra.[10]

It is felt that more positive conclusions may be obtained by a crystal structure determination, as carried out on the red compound by Hall *et al.*[9] Work in this direction is being undertaken and will be reported later.

Acknowledgement—The authors acknowledge the partial assistance of the United States Atomic Energy Commission in supporting the investigation described herein under Contract AT(11-1)582.

Zusammenfassung—Frühere Untersuchungen zeigten, daß aus homogener Lösung zwei verschiedene Uranchelate von 8-Hydroxychinolin gefällt werden können. Bei pH 5,0 erhält man dunkelrotes

$$UO_2(C_9H_6NO)_2{\cdot}C_6H_6NOH,$$

bei pH 6,8 orangefarbiges $[UO_2(C_9H_6NO)_2]_2{\cdot}C_9H_6NOH$; das *normale* Chelat $UO_2(C_9H_6NO)_2$ ist grün. Die Infrarotspektren der solvatisierten Verbindungen wurden im Bereich 5000 — 250 cm^{-1}, das des normalen Chelats von 5000 — 650 cm^{-1} aufgenommen. Aus den Spektren wird geschlossen, daß die solvatisierten Chelate sehr ähnliche Struktur besitzen.

Résumé—Des recherches antérieures ont montré qu'à partir de solutions homogènes, on peut précipiter deux chélates d'uranium et de la 8-hydroxyquinoléine différents. Le précipité rouge foncé $UO_2(C_9H_6NO)_2,C_9H_6NOH$ est obtenu à pH 5,0, l'orange

$$[UO_2(C_9H_6NO)_2]_2,C_9H_6NOH$$

à pH 6,8; le chélate *normal* $UO_2(C_9H_6NO)_2$ est vert. On a examiné les spectres infra-rouges des composés solvatés entre 5000 et 250 cm^{-1}, et celui du chélate normal entre 5000 et 650 cm^{-1}. La conclusion en est que les chélates solvatés ont des structures très semblables.

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THE OXIMATION OF BIACETYL

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Summary—Spectrophotometric evidence indicates that the reaction of biacetyl with hydroxylamine proceeds through the formation of two carbinolamine intermediates. The second of these intermediates is also encountered in the reaction of biacetyl monoxime with hydroxylamine. The rate-limiting step in the oximation of biacetyl is the slow dehydration of the initially formed intermediate, as is evidenced from the various rate constants obtained for the two reactions over the range 0–10°. When nickel(II) is present in the biacetyl-hydroxylamine system, the formation of nickel dimethylglyoximate proceeds by two independent mechanisms, whereas only a single mechanism is responsible for precipitate formation in the biacetyl monoxime-hydroxylamine system.

INTRODUCTION

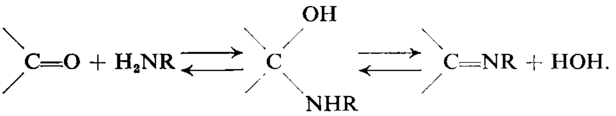
PREVIOUS studies[1–3] on the precipitation from homogeneous solution of nickel dimethylglyoximate have indicated the necessity of further study of the reaction of biacetyl and hydroxylamine to form biacetyl monoxime and dimethylglyoxime:

$$CH_3COCOCH_3 + NH_2OH \xrightarrow{k_1} CH_3C(:NOH)COCH_3 + H_2O \qquad (1)$$

$$CH_3C(:NOH)COCH_3 + NH_2OH \xrightarrow{k_2} CH_3C(:NOH)C(:NOH)CH_3 + H_2O \quad (2)$$

Since the classical studies of Barrett and Lapworth,[4] Olander,[5] Conant and Bartlett[6] and Westheimer,[7] there have been many subsequent studies of the reactions between nitrogen bases and carbonyl compounds. The results of these experiments show striking maxima in the rate-pH profiles of these reactions. This effect has been attributed to the opposing effects of the decrease in the concentration of the free nitrogen base at low pH and general acid catalysis.

Jencks[8] has shown that the rate-limiting step in the formation of oximes at neutral pH is not the attack of the nitrogen base on the carbonyl, but is the acid-catalysed dehydration of an addition compound. The reaction mechanism proposed by Jencks is:



$$\rangle C{=}O + H_2NR \rightleftharpoons \rangle C\langle^{OH}_{NHR} \rightleftharpoons \rangle C{=}NR + HOH.$$

Salesin, Abrahamson and Gordon[3] have studied the effect of pH on the reaction of hydroxylamine with biacetyl at 15·0°. These investigators found that the specific rate constants for reactions (1) and (2) were highly pH dependent, with the rates being faster at lower pH values.

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The present investigation was undertaken to determine the existence of and to study the properties of intermediates formed during the reaction between biacetyl and hydroxylamine, to determine the temperature dependence of the reaction rate constants and to note the effect of nickel(II) on the reaction sequence.

EXPERIMENTAL

Reagents

Biacetyl. PF/HS-grade biacetyl (Burdick and Jackson Laboratories, Muskegon, Mich., U.S.A.) was purified by the method of Salesin *et al.*[3]

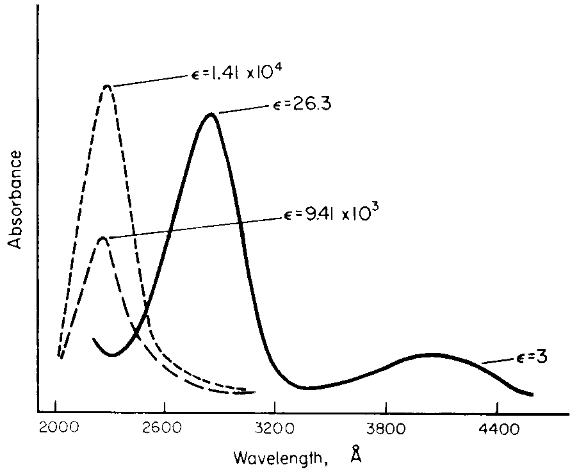


FIG. 1.—Spectra of biacetyl, biacetyl monoxime and dimethylglyoxime in aqueous NH_4Cl solution:

($pH = 7{\cdot}00$—adjusted with NH_3
$t = 5°$
$[NH_4Cl] = 7{\cdot}1 \times 10^{-2}M$)
——— Biacetyl
– – – – – Biacetyl monoxime
- - - - - - - Dimethylglyoxime.

Biacetyl monoxime. Highest-Purity-Grade biacetyl monoxime (Fisher Scientific Co., Cleveland, Ohio, U.S.A.) was triply sublimed at 35° and 1 mm of mercury.

Hydroxylamine hydrochloride. Analytical Reagent-Grade hydroxylamine hydrochloride (Fisher Scientific Co., Cleveland, Ohio, U.S.A.) was recrystallised from 95% ethanol.

All other chemicals used in the investigation were reagent grade.

Apparatus

All pH measurements were determined with a Beckman Model 9600 pH meter calibrated with a pH reference buffer solution (pH 7·00 ± 0·01) at 25° (Fisher Scientific Co.).

The spectrophotometric studies were made with a Cary Model 14 recording spectrophotometer equipped with a thermostatted cell compartment.

A Burroughs 220 computer was utilised in data-fitting computations.

Procedures

The following spectrophotometric procedures used in studying the biacetyl-hydroxylamine and the biacetyl monoxime-hydroxylamine systems in the absence and in the presence of nickel(II) utilised the spectra of Fig. 1 in order to follow the various species in the reaction solution. (The ultraviolet spectra of aqueous biacetyl monoxime, dimethylglyoxime and nickel dimethylglyoximate solutions have been reported previously.[3]) In correspondence with the conditions employed in the precipitation of nickel dimethylglyoximate,[1] the amount of hydroxylamine used in all reactions was in large excess compared to the oximes.

Series 1: The same procedure as reported by Salesin *et al.*[3] for studying the reaction between biacetyl and hydroxylamine was used in this series of experiments with the exceptions that (*a*) the pH was held constant at 7·00 ± 0·02, at 25°, and (*b*) the temperature was varied over the range 5·0° to 35·0°. The time required from mixing of reagents to the recording of the results was about 4 min.

Series 2: Exactly 0·5000 g of hydroxylamine hydrochloride was dissolved in 90 ml of water, and the pH was adjusted to 7·00 ± 0·02, at 25°; the final volume was 100·0 ml.

A portion of the hydroxylamine solution was used as the reference solution; exactly 16·00 ml, at 25°, were placed in the 5·0-cm sample cell, and the cell was placed in the thermostatted sample compartment of the Cary 14 until temperature equilibrium was reached.

A biacetyl solution was prepared by dissolving 1·545 ml, at 25°, of pure biacetyl in 100·0 ml of solution. The kinetic experiment was started when 0·050 ml of this solution (25°) was added to the hydroxylamine solution in the sample cell in the Cary 14.

The wavelength was held constant at 2838 Å. The temperature for the series was varied over the range 0·5–10·0°. The time required from mixing of reagents to the recording of the results was 0·10–0·15 min.

Series 3: The same procedure was used as described in *Series* 2 above, except that the hydroxylamine solution was replaced by an equivalent NH_4Cl-HCl solution (pH 7·00).

Series 4: The hydroxylamine solution, prepared as described in *Series* 2 above, was used as the reference solution. Exactly 3·150 ml of the solution were added to a 1·0-cm cell, and the cell was then placed in the thermostatted sample compartment.

A solution of biacetyl monoxime was prepared by dissolving 0·1497 g of the solid in 250·0 ml of solution. The kinetic experiment was started when 0·050 ml of this solution was added to the hydroxylamine solution in the sample cell.

The wavelength was held constant at 2250 Å. The temperature for the series was varied over the range 0·5–10·0°.

Series 5: The same procedure was used as described in *Series* 4 above with the modification described in *Series* 3 above.

Series 6: Exactly 1·2500 g of hydroxylamine hydrochloride were dissolved in 225 ml of water, and 4·146 ml of $1{\cdot}674 \times 10^{-2}M$ nickel(II) solution were added. The pH of this solution was adjusted to 7·00 ± 0·02, at 25°, and the solution was diluted to 250·0 ml.

A portion of the hydroxylamine-nickel solution was used as the reference solution. Exactly 16·00 ml, at 25°, of the hydroxylamine-nickel solution were placed in a 5·0-cm cell, and the cell was placed in the thermostatted sample compartment.

The experiment was started when 0·050 ml of a biacetyl solution, prepared as previously described, was added to the hydroxylamine-nickel solution in the sample cell in the Cary 14.

The wavelength was held constant at 3600 Å. The temperature for the series was varied over the range 0·5–10·0°.

Series 7: Exactly 0·5000 g of hydroxylamine hydrochloride was dissolved in 90 ml of water, and 0·281 ml of $1{\cdot}674 \times 10^{-2}M$ nickel(II) solution was added. The pH of this solution was adjusted to 7·00 ± 0·02, at 25°, and the solution was diluted to 100·0 ml.

A portion of this solution was used as the reference solution. Exactly 3·150 ml of it were placed in a 1·0-cm cell, and the cell was then placed in the thermostatted sample compartment.

The experiment was started when 0·050 ml of a solution of biacetyl monoxime, prepared as previously described, was added to the hydroxylamine-nickel solution in the sample cell in the Cary 14.

The wavelength was held constant at 2250 Å. The temperature for the series was varied over the range 0·5–10·0°.

RESULTS AND DISCUSSION

Series 1

The results of the experiments are shown in Fig. 2 and Table I. The values of k_1 and k_2 [the rate constants of equations (1) and (2)] were calculated using the mathematical model and approximations previously proposed.[3]

As can be seen from Table I, the values of the rate constants, obtained by the use of approximations, show deviations at each temperature. To eliminate the approximations, a computer programme was utilised in which the best values of the rate constants were determined by numerically fitting the experimental results. The results of the re-analysis again confirmed the values of k_1 shown in Table I. Further, (*a*) the changes in k_2 were even more random with respect to temperature change and (*b*) the numerical fit to the curves of Fig. 2 became poorer as the temperature was lowered. Reliable values of k_2 simply could not be obtained by numerical analysis because of the insensitivity of the calculated absorbance values to changes in the trial values of this parameter. However, a direct way to arrive at values for k_2 was to arrange a series of experiments, similar to the biacetyl-hydroxylamine series, with the biacetyl replaced by biacetyl monoxime. From the previous model, one would predict the

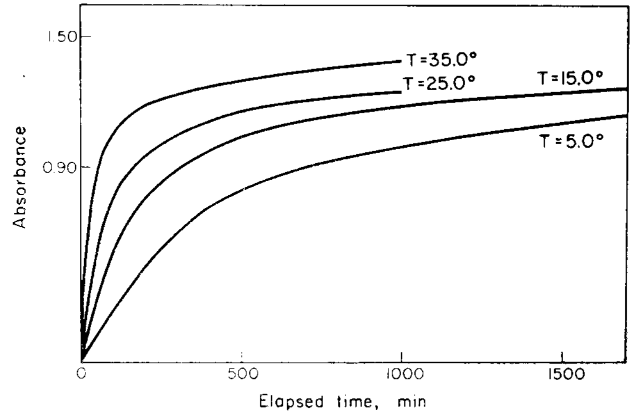


Fig. 2.—Absorbance *versus* time for the continuous spectrophotometric monitoring of the biacetyl-hydroxylamine system

([Biacetyl] = $1{\cdot}080 \times 10^{-4}M$
[Hydroxylamine] = $7{\cdot}194 \times 10^{-2}M$
$\lambda = 2250$ Å).

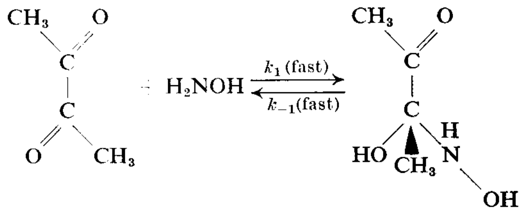
absorbance versus time dashed curve shown in Fig. 3, whereas the solid curve of Fig. 3 shows the results observed at 5·0°.

The observation of Fig. 3, coupled with (*a*) the poorer numerical fit of the results as the temperature was lowered and (*b*) a non-linear Arrhenius plot for the specific rate constant k_1 of *Series* 1, indicated that the model[3] used for the biacetyl-hydroxylamine system was inadequate to explain the observed results.

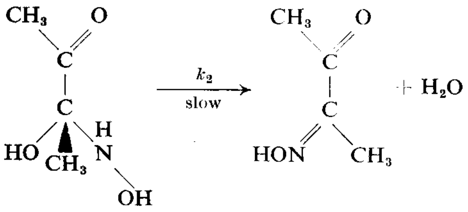
Series 2 *and* 3

Because it was not possible to obtain reliable values of k_1 and k_2 from the observations of *Series* 1, the experiments of *Series* 2 and 3 were devised to follow the concentration of biacetyl rather than biacetyl monoxime and dimethylglyoxime. The results are shown in Fig. 4.

To explain qualitatively the observations shown in Fig. 4, the following model, incorporating Jencks' concept of a reaction intermediate, was formulated:



(3)



(4)

or in abbreviated notation:

$$B + H \underset{k_{-1}(\text{fast})}{\overset{k_1(\text{fast})}{\rightleftarrows}} I_1 \tag{3a}$$

$$I_1 \xrightarrow[\text{slow}]{k_2} M + H_2O \tag{4a}$$

Initially, the concentration of I_1 is zero. If the extinction of I_1 is larger than that of biacetyl at 2838 Å, then the rapid initial increase of the absorbance can be explained by the rapid formation of I_1 (see Fig. 4, part A of curve). However, as the concentration of I_1 increases, the reverse rate increases and the over-all rate formation of I_1 decreases. Thus, the rate of absorbance-increase decreases (see Fig. 4, part B of curve). When the rate of formation of I_1 becomes less than the rate of formation of biacetyl monoxime [near equilibrium for reaction (3)] the absorbance of the system decreases (see Fig. 4, part D of curve).

TABLE I.—RESULTS OF THE PRELIMINARY KINETIC STUDIES IN THE BIACETYL-HYDROXYLAMINE SYSTEM

Temp., °C	$k_1(\times 10^1)$, $l.mole^{-1}.min^{-1}$	$k_2(\times 10^3)$, $l.mole^{-1}.min^{-1}$
5·0	0·195	8·47
	0·236	7·90
	0·393	5·73
15·0	0·975	5·87
	0·870	4·37
	0·790[a]	2·80[a]
25·0	1·81	8·81
	1·75	8·55
35·0	3·99	6·44
	8·09	26·3

[a] Calculated from the results of Salesin *et al.*[3]

Attempts to extract the postulated long-lived intermediate carbinolamine into several organic phases were unsuccessful. However, direct proof of the presence of the intermediate was obtained by observing an absorbance maximum in the ultraviolet spectrum not associated with any of the known reactants or products. The position of this absorbance maximum, initially at 2320 Å, varied with time, the shift being toward shorter wavelengths. The extinction coefficient, ε_{I_1}, of the intermediate and the rate constant, k_1, associated with equation (3) were obtained by the following numerical analysis.

From equations (3) and (4) the following may be written:

$$\frac{dA}{dt} = l\left[\varepsilon_B \frac{dB}{dt} + \varepsilon_{I_1} \frac{dI_1}{dt} + \varepsilon_M \frac{dM}{dt}\right] \tag{5}$$

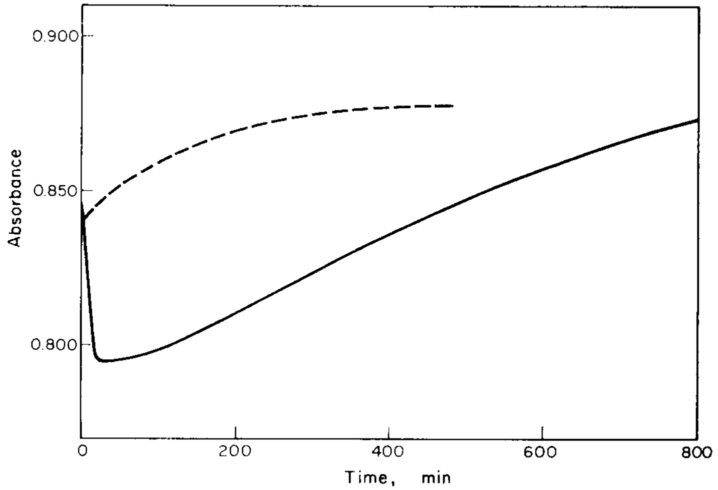


FIG. 3.—Absorbance *versus* time, expected and found, for the biacetyl monoxi
hydroxylamine system
([Biacetyl monoxime] = 8.94 × $10^{-5}M$
[Hydroxylamine] = 7·19 × $10^{-2}M$
t = 5·00°
λ = 2275 Å
pH = 7·0).

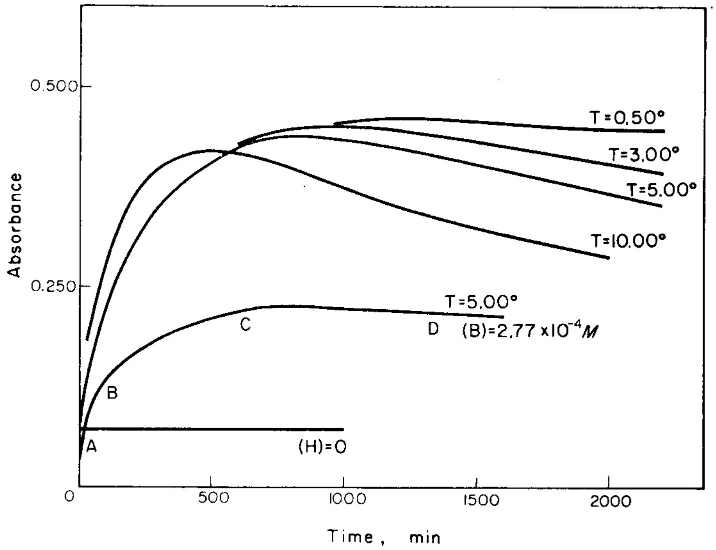


FIG. 4.—Absorbance *versus* time for the biacetyl-hydroxylamine system
([Biacetyl] = 5·537 × $10^{-4}M$
[Hydroxylamine] = 7·193 × $10^{-2}M$
λ = 2838 Å).

where B, I_1 and M = solution concentrations of biacetyl, intermediate I_1 and biacetyl monoxime, respectively;
ε_B, ε_{I_1}, and ε_M = extinction coefficients of biacetyl, intermediate I_1 and biacetyl monoxime, respectively;
A = total absorbance of the solution;
l = path length of the solution in cm;
t = time in min;
k_1, k_{-1}, k_2 = specific rate constants for reactions (3) and (4).

When t is very small, the value of dM/dt and the rate of the reverse reaction (3) will be zero. Further, it was experimentally noted that the initial rapid absorbance increase is first order with respect to biacetyl, *i.e.*, $(dA/dt)_B = 2(dA/dt)_{B/2}$ and $(dA/dt)_H = 2(dA/dt)_{H/2}$. Therefore, equation (5) can be integrated as follows:

$$A = l\{B_0[1 - \exp(-k_1't)]\varepsilon_{I_1} + [B_0 \exp(-k_1't)]\varepsilon_B\} \qquad (6)$$

where B_0 = initial concentration of biacetyl.
Equation (6) contains two unknowns, *i.e.*, k_1' and ε_{I_1}. To obtain their values another equation was derived from equation (5) by neglecting $(\Delta B/\Delta t)\varepsilon_B$, the smaller term, because ε_B is much smaller than ε_{I_1},

$$k_1' = \frac{\Delta A}{(\Delta t)(\varepsilon_{I_1})(\bar{B})l} \qquad (7)$$

where $k_1' = k_1(H)$;

$\bar{B}$ = average concentration of biacetyl over the time interval Δt.
Then, equations (6) and (7) were used in an iterative calculation to arrive at k_1' and ε_{I_1}, the best values for which are 0·053/min, at 5·0°, and $\frac{200(\text{Abs units})(\text{litre})}{(\text{cm})(\text{mole})}$, respectively.

With this value for ε_{I_1} and with the averaged results (5 runs) obtained at 3·0°, the value of k_1' at 3·0° was calculated to be 0·0509/min from equation (6).

At 0·5°, the results were too uncertain during the initial minutes of the reaction to be used for calculations of k_1'. At 10·0°, the initial reaction took place too quickly to gain reliable results with the experimental techniques employed in this investigation.

If it is assumed that the concentration of the biacetyl monoxime is zero during the early stages of the reaction, the following equation for k_{-1} can be derived from equations (5) and (6):

$$k_{-1} = \frac{\dfrac{\frac{\Delta A}{\Delta t}}{(\varepsilon_{I_1} - \varepsilon_B)l} - k_1'\left[\dfrac{\bar{A} - B_0\varepsilon_{I_1}l}{(\varepsilon_B - \varepsilon_{I_1})l}\right]}{\dfrac{\bar{A} - B_0\varepsilon_{I_1}l}{(\varepsilon_B - \varepsilon_{I_1})l} - B_0} \qquad (8)$$

Table II shows the results of the calculation of k_{-1} obtained by using the averaged values at 3·0° and 5·0° over various reaction time intervals.

The calculation of k_2 [*cf.* equation (4)] is based on the assumption that the absorbance change during part D of the curve shown in Fig. 4 results from reaction (4) only. The following equations are based on this assumption:

$$\ln I_1 = -k_2 t + \ln (I_1)_0 \qquad (9)$$

TABLE II.—RESULTS OF THE CALCULATION OF k_{-1} AT 3·0° AND 5·0°

Temp. = 3·0°		Temp. = 5·0°	
min	k_{-1}, *min*$^{-1}$	*min*	k_{-1}, *min*$^{-1}$
7·5	0·00292	8·0	0·00494
10·0	0·00480	10·0	0·00519
12·5	0·00590	12·0	0·00478
17·5	0·00685	20·0	0·00811
20·0	0·00875	22·0	0·00816
22·5	0·01120	24·0	0·00648
27·5	0·01120	32·0	0·00755
30·0	0·01010	34·0	0·00805
32·5	0·01118	36·0	0·00686
37·5	0·01006	52·5	0·00550
40·0	0·00951	55·0	0·00552
42·5	0·00918	57·5	0·00555
47·5	0·00912	65·0	0·00559
50·0	0·00884	67·5	0·00532
52·5	0·00819	70·0	0·00524
57·5	0·00870	77·5	0·00516
60·0	0·00831	80·0	0·00539
62·5	0·00727	82·5	0·00520
67·5	0·00792	110·0	0·00500
70·0	0·00725	115·0	0·00479
72·5	0·00673	120·0	0·00493
77·5	0·00680		
80·0	0·00647	mean	= $0{\cdot}0058_7$
82·5	0·00615		
87·5	0·00626		
90·0	0·00651		
92·5	0·00692		
97·5	0·00637		
100·0	0·00637		
102·5	0·00638		
105·0	0·00632		
110·0	0·00601		
115·0	0·00565		
120·0	0·00573		
125·0	0·00566		
mean	= $0{\cdot}0074_2$		

where $(I_1)_0$ = initial concentration of I_1
Because $A = kI_1$

$$\ln A = -k_2 t + \ln A_0 \qquad (10)$$

Thus, as can be seen from equation (10), a plot of the *logarithm of the absorbance versus time* should be linear with a slope equal to $-k_2$. Fig. 5 shows such plots for the results obtained at 0·5, 3·0, 5·0 and 10·0° with values of k_2 given in Table III. [The plots shown in Fig. 5 can also be used to obtain a value of ε_{I_1}. By extrapolating to time zero, where $A_0 = \varepsilon_{I_1}(I_1)_0 l$, and assuming $(I_1)_0 = B_0$, the value of ε_{I_1} found was 199, in good agreement with the value of 200 found previously.]

Table III shows the energy of activation calculated from the temperature dependence of the various specific rate constants. The value of the energy of activation obtained from the specific rate constant, k_1, of the Salesin model is 16 Kcal per mole. A comparison of the two models for the system is shown below:

Model by Salesin et al.[3]

$$B + H \xrightarrow{\Delta E_1^* = 16\text{Kcal/mole}} I_A^* \rightarrow M \tag{11}$$

Present model

$$B + H \xrightarrow{\Delta E_2^* = 3.1\text{ Kcal/mole}} I_B^* \xrightarrow{\Delta E_3^* \cong 0}$$

$$I_1 \xrightarrow{\Delta E_4^* = 12.9\text{ Kcal/mole}} I_C^* \rightarrow M \tag{12}$$

where I_n^* = an activated complex (n = A, B, C);
ΔE_n^* = energy of activation (n = 1, 2, 3, 4).

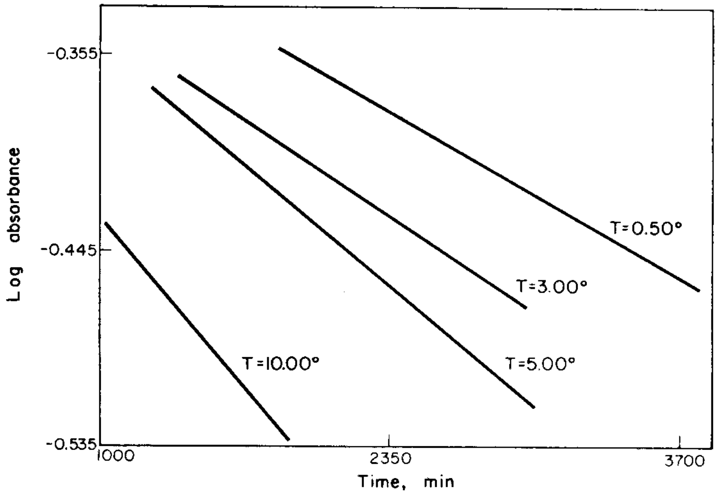
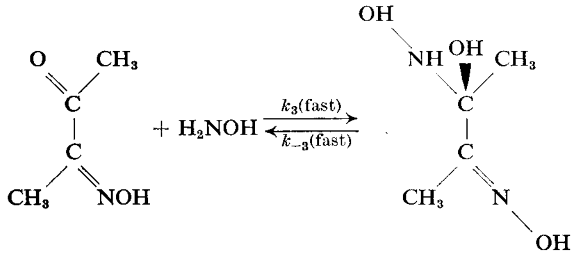


FIG. 5.—Log_{10} absorbance *versus* time for the biacetyl-hydroxylamine system.

Within the limits of experimental error, ΔE_3^* was found to be nearly zero. Thus, the total energy barrier in the formation of biacetyl monoxime from biacetyl and hydroxylamine is the same for both models. Furthermore, the activated complexes I_A^* and I_C^* must be identical, and they represent the structure with the highest energy in the system.

Series 4 *and* 5

The results of these series, shown in Fig. 6, can be qualitatively explained by again using the proposed carbinolamine intermediate as shown below:



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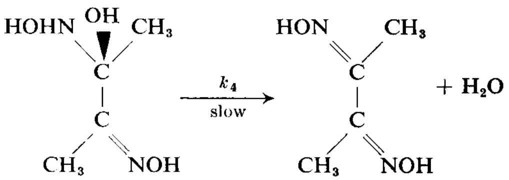

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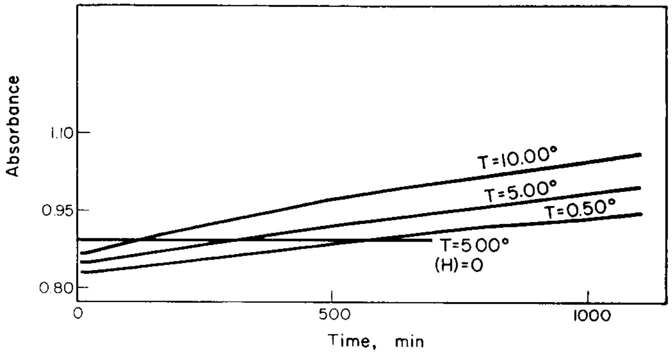

FIG. 6.—Absorbance *versus* time for the biacetyl monoxime-hydroxylamine system ([Biacetyl monoxime] = $9{\cdot}254 \times 10^{-5}M$ [Hydroxylamine] = $7{\cdot}082 \times 10^{-2}M$ $\lambda = 2250$ Å).

or in abbreviated form:

$$M + H \underset{k_{-3}(\text{fast})}{\overset{k_3(\text{fast})}{\rightleftarrows}} I_2 \tag{13a}$$

$$I_2 \xrightarrow[\text{slow}]{k_4} D + H_2O \tag{14a}$$

where I_2 and D = solution concentrations of intermediate I_2 and dimethylglyoxime, respectively;

k_3, k_{-3} and k_4 = specific rate constants for reactions 13 and 14, respectively.

The proposed reaction sequence for the biacetyl monoxime-hydroxylamine system was again tested by scanning the ultraviolet spectrum just after mixing the reactants, and an absorbance maximum, not associated with biacetyl monoxime or dimethylglyoxime, was observed. The position of the peak, initially at 2300 Å, varied with time, the shift being towards shorter wavelengths. A method suitable for the calculation of k_3 and k_{-3} was not found. Because of the very large values of the various extinction coefficients, the approximations used in the biacetyl-hydroxylamine system were not applicable to the biacetyl monoxime-hydroxylamine system. The calculation of k_3 must be done from observations made during the initial rapid drop in the absorbance. In as much as most of the initial absorbance change has taken place before the first results are observed, reliable values of k_3 could not be obtained. Without k_3, k_{-3} cannot be calculated from the results observed at a later and more accessible reaction time interval.

During the latter stages of the reaction, reaction (14) becomes predominant. Thus, the absorbance change is caused primarily by the changes in concentration of the intermediate, I_2, and dimethylglyoxime. The total absorbance of the reaction mixture at any time can be expressed as:

$$A = l[\varepsilon_M M + \varepsilon_{I_2} I_2 + \varepsilon_D D] \tag{15}$$

where ε_{I_2} and ε_D = extinction coefficients of intermediate I_2 and dimethylglyoxime, respectively.

If the concentration of biacetyl monoxime is some small fixed amount after 1000 min of reaction, equation (15) can be rewritten as

$$I_2 = \frac{A - C_1}{C_2} \tag{16}$$

where $C_1 = M_0\varepsilon_D l + M(\varepsilon_M l - \varepsilon_D l)$
$C_2 = \varepsilon_{I_2} l - \varepsilon_D l$

A plot of $log \left[\frac{A - C_1}{C_2}\right]$ *versus time* should be a straight line with a slope of $-k_4/2{\cdot}303$. Such a plot is shown in Fig. 7 with the values of k_4 given in Table III.

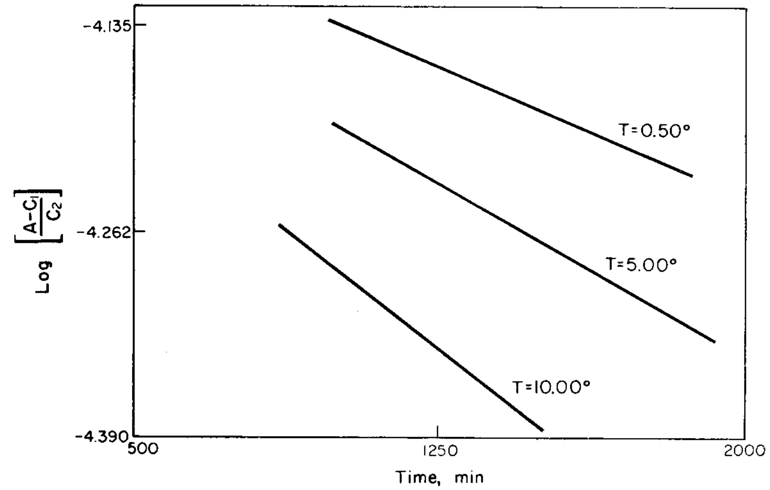

FIG. 7.—Log $\left[\frac{A - C_1}{C_2}\right]$ *versus* time for the biacetyl monoxime-hydroxylamine system.

TABLE III.—RESULTS OBTAINED DURING THE STUDY OF THE FORMATION OF DIMETHYLGLYOXIME

Rate constant, *min*$^{-1}$	Temperature, °*C* 0·5	3·0	5·0	10·0	E*, *Kcal/mole*
$k_1'(\times 10^2)$	—	5·09	5·30	—	3·1
$k_{-1}(\times 10^3)$	—	7	6	—	—
$k_2(\times 10^4)$	1·28	1·46	1·89	2·63	12·9
$k_4(\times 10^4)$	2·1	—	3·3	4·6	13

A summary of all the kinetic results obtained during the study of the formation of dimethylglyoxime from biacetyl and hydroxylamine in the absence of nickel(II) is shown in Table III.

Salesin *et al.*[3] reported that the over-all rate of the formation of biacetyl monoxime was faster than the rate of formation of dimethylglyoxime in the biacetyl-hydroxylamine system. Accordingly, the solution concentration of the biacetyl monoxime should increase to some maximum value and then decrease as the dimethylglyoxime is formed.[9] However, this was not observed in the present investigation, and the difference can be easily explained. To determine biacetyl monoxime and dimethylglyoxime, Salesin used a separational procedure in which the reaction mixture was acidified.[3] As a result, all of the I, present in the mixture was immediately converted to biacetyl monoxime[8] and thus reported as such. (The same reasoning also applies to the intermediate I_2 and dimethylglyoxime.)

Series 6 and 7

The results are shown in Figs. 8 and 9, respectively. The two absorbance maxima at t = 3·00° in Fig. 8 are the "nucleation bursts" (appearance of nickel dimethylglyoximate) reported by Salesin.[3] At 5·00° these maxima have overlapped so that only a break appears in the curve. In Fig. 9, a single nucleation burst is evident by the change of slope at about 170 min in the curves obtained at $\lambda = 2250$ Å; this is confirmed even more strikingly at 3600 Å, where only nickel dimethylglyoximate absorbs.

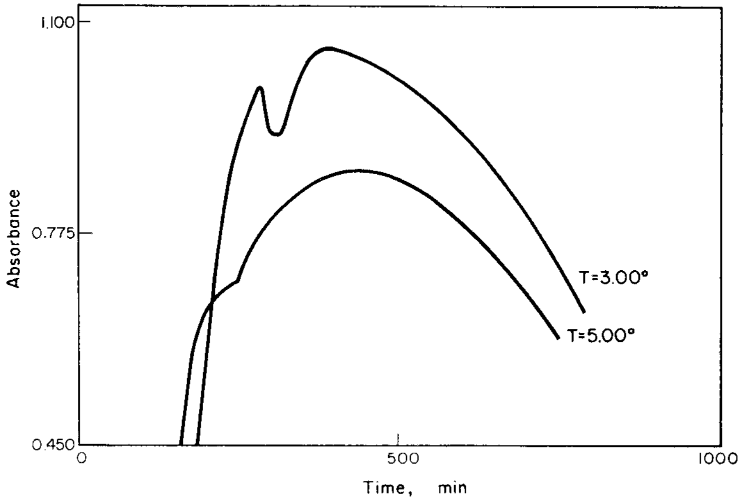

FIG. 8.—Absorbance *versus* time for the biacetyl-hydroxylamine-nickel system
([Biacetyl] = $5{\cdot}537 \times 10^{-4}M$
[Hydroxylamine] = $7{\cdot}193 \times 10^{-2}M$
$\lambda = 3600$ Å) [Ni(II)] = $2{\cdot}77 \times 10^{-4}M$.

A comparison of the large initial absorbance of the system in Fig. 6, where nickel(II) is absent, with the comparably large initial absorbance of the system in Fig. 9, where nickel(II) is present, shows the virtual absence of the lesser absorbing nickel monoxime complex. Further, a change in the nickel concentration by a factor of one-half in the two systems of Figs. 8 and 9 had no effect on the absorption curves, and hence on the rate-controlling reaction. Thus, it was concluded from these two observations that the absorbance change of the system of Fig. 9 was the result of the following reaction sequence:

$$\mathrm{M} + \mathrm{H} \underset{k_{-3}(\text{fast})}{\overset{k_3(\text{fast})}{\rightleftarrows}} \mathrm{I}_2 \tag{13a}$$

$$\mathrm{I}_2 \xrightarrow[\text{slow}]{k_4} \mathrm{D} + \mathrm{H_2O} \tag{14a}$$

$$2\mathrm{D} + \mathrm{Ni(II)} \xrightarrow{\text{fast}} \mathrm{NiD_2} + 2\mathrm{H^+} \tag{17}$$

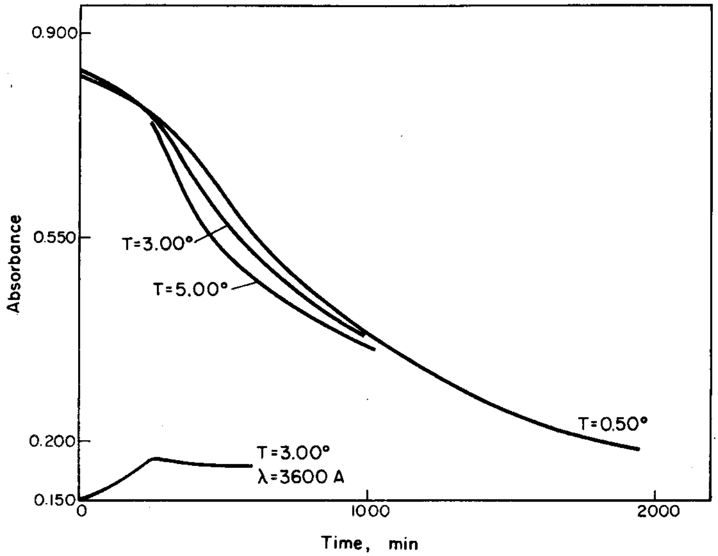

FIG. 9.—Absorbance *versus* time for the biacetyl monoxime-hydroxylamine-nickel system

([Biacetyl monoxime] = 9·254 × $10^{-5}M$
[Hydroxylamine] = 7·082 × $10^{-2}M$
[Ni(II)] = 4·625 × $10^{-5}M$
λ = 2250 Å).

the last equation being responsible for the over-all absorbance decrease. Values of k_4 were obtained from the slope of *log absorbance (2250 Å) versus time* from the first 170-min portion of two of the curves of Fig. 9. These compare with previous values as shown in Table IV:

TABLE IV

Temperature, °*C*	k_4, *min*$^{-1}$	
	Ni(II) absent	Ni(II) present
0·5°	2·1 × 10^{-4}	2·5 × 10^{-4}
5·0°	3·3 × 10^{-4}	3·3 × 10^{-4}

The very close agreement of the values of k_4 in the two systems shows that nickel(II) has no effect on the dehydration of the carbinolamine intermediate I_2, *i.e.*, the rate-controlling reaction.

Extension of this conclusion to the biacetyl-hydroxylamine-nickel(II) system leads in a similar way to the following reaction sequence,

$$B + H \underset{k_{-1}(\text{fast})}{\overset{k_1(\text{fast})}{\rightleftharpoons}} I_1 \tag{3a}$$

$$I_1 \xrightarrow[\text{slow}]{k_2} M + H_2O \tag{4a}$$

$$M + H \underset{k_{-3}(\text{fast})}{\overset{k_3(\text{fast})}{\rightleftharpoons}} I_2 \tag{13a}$$

$$I_2 \xrightarrow[\text{slow}]{k_4} D + H_2O \tag{14a}$$

$$2D + Ni(II) \xrightarrow{\text{fast}} NiD_2 \downarrow + 2H^+ \tag{17}$$

where the slowest step is the dehydration of I_1 (*cf.* Table III). If the reaction sequence is valid, then a plot of *log absorbance (3600 Å) versus time* for the first 120 min of Fig. 8 should be linear with slope equal to k_2. The values of k_2 thus obtained compare with previous values as shown in Table V:

TABLE V

Temperature, °*C*	k_2, *min*$^{-1}$	
	Ni(II) absent	Ni(II) present
3·0°	$1{\cdot}46 \times 10^{-4}$	$1{\cdot}2 \times 10^{-2}$
5·0°	$1{\cdot}89 \times 10^{-4}$	$2{\cdot}2 \times 10^{-2}$

The change in the values of k_2 by a factor of 100 shows clearly that nickel(II) must play a significant role in the previous reaction sequence, *i.e.*, numbers [(3a) to (14a) inclusive], in as much as nickel dimethylglyoximate is produced at a rate far faster than is indicated by the rate of formation of dimethylglyoxime from biacetyl and hydroxylamine only.

Because nickel(II) has already been shown to have little effect on the biacetyl monoxime-hydroxylamine part of the reaction sequence, it must then exert its influence by complexing with the intermediate I_1. From the following results from Table III and the previous values of k_2, (repeated in Table VI),

TABLE VI

Temperature	k_1', *min*$^{-1}$	k_2, *min*$^{-1}$
	Ni(II) absent	Ni(II) present
3°	$5{\cdot}09 \times 10^{-2}$	$1{\cdot}2 \times 10^{-2}$
5°	$5{\cdot}30 \times 10^{-2}$	$2{\cdot}2 \times 10^{-2}$

it can be seen that the over-all rates of formation of I_1 and nickel dimethylglyoximate are comparable in the two systems, *i.e.*, biacetyl-hydroxylamine and biacetyl-hydroxylamine-nickel(II), respectively. Thus, in the latter system, the rate-limiting step must be the formation of I_1 [*cf.* equation (3a)]; I_1 is then immediately complexed by nickel(II). Furthermore, the complex must then proceed, by a series of very fast reactions, all involving nickel complexes, to the end product, nickel dimethylglyoximate. These conclusions now provide an explanation for the multiple nucleation bursts initially reported by Salesin[3] (*cf.* two absorption maxima of Fig. 8); this is in contrast to the single burst observed in the system of Fig. 9.

In the biacetyl-hydroxylamine-nickel(II) system, there is not only the complex between nickel(II) and I_1 as follows,

$$Ni^{2+} + I_1 \rightleftharpoons NiI_1^+ + H^+ \tag{18}$$

but also likely the following complex.

$$NiI_1^+ + I_1 \rightleftharpoons Ni(I_1)_2 + H^+ \tag{19}$$

Some of the NiI_1^+ complex may be converted, by dehydration of the intermediate and further reaction with hydroxylamine, to NiD^+. The latter complex will have to wait for additional dimethylglyoxime to be produced by the slow reaction sequence involving biacetyl and hydroxylamine in order to precipitate nickel dimethylglyoximate. The $Ni(I_I)_2$ complex is also converted by dehydration to NiD_2. In addition to this over-all path in which the two nickel carbinolamine intermediates are involved in the precipitation of nickel dimethylglyoximate by equations (18) and (19), there is another independent path. This path involves precipitation of the solid red chelate by equation (17). Thus, there are at least two independent paths giving rise to the two nucleation bursts. In contrast to this, there can be only one path, hence one nucleation burst, with the reaction sequence involving biacetyl monoxime and hydroxylamine.

Acknowledgment—The authors wish to acknowledge the partial support of the United States Atomic Energy Commission under Contract At-(11-1)-582. One of the authors (O. E. H., Jr.) acknowledges a National Aeronautics and Space Administration traineeship during 1963–4.

Zusammenfassung—Spektralphotometrische Ergebnisse zeigen, daß die Reaktion von Biacetyl mit Hydroxylamin über zwei Carbinolamin-Zwischenstufen verläuft. Das zweite von diesen Zwischenprodukten findet man auch bei der Reaktion von Bicetylmonoxim mit Hydroxylamin. Der geschwindigkeitsbestimmende Schritt bei der Oximierung von Biacetyl ist die langsame Dehydratation des ersten Zwischenprodukts, wie aus den verschiedenen Geschwindigkeitskonstanten für die zwei Reaktionen zwischen 0 und 10° hervorgeht. Bei Gegenwart von Nickel im Biacetyl-Hydroxylamin-System geht die Bildung von Nickel-Dimethyl-glyoximat nach zwei unabhängigen Mechanismen vor sich; dagegen ist nur ein Mechanismus für die Neiderschlagsbildung im Biacetylmonoxim-Hydroxylamin-System verantwortlich.

Résumé—Des preuves spectrophotométriques montrent que la réaction du diacétyle avec l'hydroxylamine passe par la formation de deux carbinolamines intermédiaires. On rencontre également le second de ces intermédiaires dans la réaction de la diacétyle-monoxime avec l'hydroxylamine. Le stade qui limite la vitesse d'oximation du diacétyle est la déshydratation lente de l'intermédiarie initialement formé. Ceci est mis en évidence par les diverses constantes de vitesse obtenues pour les deux réactions entre 0 et 10°. Lorsque le nickel(II) est présent dans le système diacétyle-hydroxylamine, la formation de diméthylglyoximate de nickel procède par deux mécanismes indépendants, cependant qu'un seul mécanisme est responsable de la formation du précipité dans le système diacétyle-monoxime-hydroxylamine.

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SPECTROPHOTOMETRIC DETERMINATION OF COPPER WITH POLYAMINOCARBOXYLIC ACIDS

ETHYLENEDIAMINE-N,N′-DI-α-PROPIONIC ACID

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Summary—A new method for the spectrophotometric determination of copper with polyaminocarboxylic acids is presented. The ligand chosen is ethylenediamine-N,N′-di-α-propionic acid (EDDPA) which compares favourably, in sensitivity and selectivity, with all the other similar compounds previously proposed. The copper complex absorbs at 670 mμ with a molar extinction coefficient of 140 at any pH between 3 and 8. Beer's law is obeyed over the range 0–400 ppm of copper and the temperature and ionic strength do not adversely affect the method. Nickel interferes when present in comparable or greater amounts than copper.

INTRODUCTION

Several methods for the spectrophotometric determination of copper with polyaminocarboxylic acids have been proposed in the past few years. These methods have several advantages over the spectrophotometric procedures using diethyldithiocarbamate, dithio-oxamide or dithizone, such as greater simplicity and rapidity, few interferences, wide range of suitable pH, high stability and solubility of the complexes formed. The main inconvenience is their low sensitivity, the limit being about 10 ppm of copper, but this is not very important in routine problems of copper analysis, when this element is present in appreciable percentages.

Nitrilotriacetic acid (NITA),[1] ethylenediaminetetra-acetic acid (EDTA),[2] 1,2-diaminocyclohexanetetra-acetic acid (DCTA),[3] ethyleneglycol-bis(β-aminoethylether)-tetra-acetic acid (EGTA)[4] and 2,2′-diaminodiethylethertetra-acetic acid (EEDTA)[5] have all been suggested as spectrophotometric reagents for copper. These substances are all potentially hexadentate ligands, excepting NITA, which is tetradentate and forms tetrahedral complexes if it is the sole ligand in the co-ordination sphere.

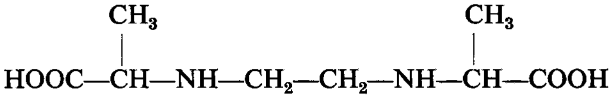
Although the intensity of the colour is not directly related to the type of structure, it is somewhat surprising that no complexan has been suggested with the property of forming square-planar complexes when completely co-ordinated, because it is known that the cupric ion has a marked tendency to such arrangements.

The obvious choice would be ethylenediamine, N,N′-diacetic acid (EDDA), (I), which is, however, rather difficult to prepare, because of the easy replacement of the hydrogen atoms bonded to nitrogen

$$HOOC—CH_2—HN—CH_2—CH_2—NH—CH_2—COOH$$

I

Not long ago, Irving, Shelton and Evans studied a sterically hindered complexing reagent derived from EDDA[6] and differing from it by having α-propionate instead of acetate groups (II)



$$HOOC-\overset{CH_3}{\overset{|}{C}}H-NH-CH_2-CH_2-NH-\overset{CH_3}{\overset{|}{C}}H-COOH$$

II

This reagent, ethylenediamine-N,N′-di-α-propionic acid (EDDPA), gives complexes only slightly less stable than EDDA and is far easier to prepare. Indeed, the two α-methyl groups hinder the replacement of the remaining hydrogen atoms bonded to nitrogen and furthermore the compound is easily obtained in a fair state of purity.

Ethylenediamine-N,N′-di-α-propionic acid intensifies the blue colour of dilute copper solutions more strongly than similar complexing agents.

COMPARISON WITH OTHER METHODS

The sensitivity of the present method relative to procedures using other polyaminocarboxylic acids is best appreciated by examining the maximum values of the molar extinction coefficients of the respective copper complexes. We have investigated the variation of absorbance with pH for several complexans, using 100% excess of each compound relative to copper, and have calculated the required ε_{max} values without taking into account the possibility of equilibria between different complexes. The calculated extinction coefficients are summarised in Table I; the absorption curves of several of the copper complexes, at a suitable value of pH, are presented in Fig. 1.

Table I.—Molar extinction coefficients of copper complexes

Ligand	pH	λ_{max}(mμ)	ε_{max}
NITA	—	775 880	54* 60
EDTA	7	735	91
MEDTA	6	735	106
DCTA	2·5	680	118
EEDTA	1·5	720	59
EGTA	6	700	68
HCEDTA	12·5	735	133
EDDPA	6	670	140

* From ref. 9.

The following abreviations are used:

EDTA	ethylenediaminetetra-acetic acid
MEDTA	1,2-diaminopropanetetra-acetic acid (methyl-EDTA)
DCTA	1,2-diaminocyclohexanetetra-acetic acid

EGTA	ethyleneglycol-bis(β-aminoethylether)tetra-acetic acid
HCIDA	2-hydroxycyclohexyliminodiacetic acid
HCEDTA	N-hydroxycyclohexylethylenediaminetriacetic acid
EEDTA	ethyletherdiaminotetra-acetic acid
EDDPA	ethylenediamine-NN′-di-α-propionic acid
ADA	anthranyldiacetic acid
IMDA	iminodiacetic acid
UDA	uramildiacetic acid
NITA	nitrilotriacetic acid

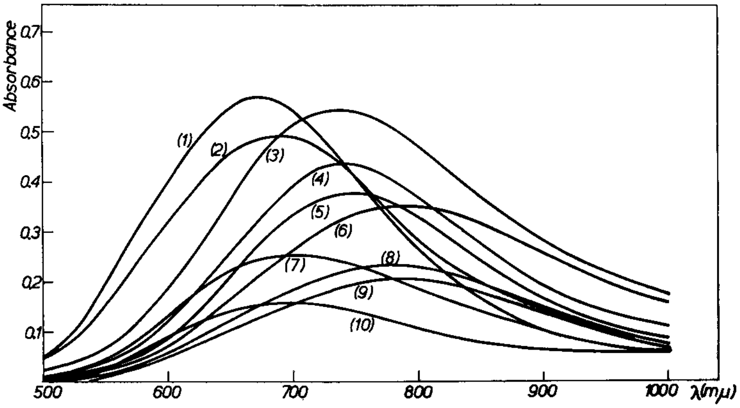


FIG. 1.—Absorption curves of the copper complexes of some polyaminocarboxylic acids (concentration of copper 0·004*M*; concentration of the ligand 0·008*M*):
(1) EDDPA, (2) DCTA, (3) HCEDTA, (4) MEDTA, (5) EDTA, (6) HCIDA, (7) EGTA
(8) ADA, (9) UDA, (10) IMDA.

Although the extinction coefficients found are not very accurate, because the commercial complexans were not further purified and the instrument used is not adequate for precise measurements, the values obtained confirm our hypothesis by showing that EDDPA is indeed the most sensitive of all the reagents studied. DCTA and HCEDTA also have interesting possibilities, at low and high pH values, respectively.

Bermejo-Martínez and Blas-Pérez[5] have pointed out the advantages of EEDTA for work at low pH, but the extinction coefficient of the copper complex of this ligand is small, and the method, consequently, not very sensitive. Hence, although the limit of pH when using DCTA cannot be so low and needs a rather accurate adjustment, this reagent, also proposed by the same authors, still seems to have advantages relative to EEDTA.

HCEDTA seems to be the appropriate complexan for work at high pH and it will be dealt with in a future paper. The increasing absorption with pH probably results from the ionisation of the phenolic hydrogen which alters the environment of the copper atom. The same is found for the HCIDA-copper-complex.

The absorption curves in Fig. 1 seem to fall into three groups, absorbing in limited ranges of wavelength, corresponding to a definite type of complexan.

Thus, EDDPA probably forms planar complexes and its copper complex absorbs at 670 mμ; EDTA, MEDTA and HCEDTA probably form weakly tetragonal complexes and absorb between 725 and 745 mμ; ADA, UDA and HCIDA absorb between 770 and 790 mμ and may form copper complexes more close to cubic symmetry; finally, EGTA behaves like IMDA, both absorbing at 690 mμ which is close to the value found for EDDPA; they probably also form planar complexes having one co-ordination site occupied by a water molecule. In the case of EGTA this should be ascribed to the 2:1 complex.[7] The maximum of absorption at 680 mμ found for DCTA at pH 2·5 may also correspond to the planar complex with two free carboxylic acid groups.

The behaviour of NITA resembles that of other similar tetradentate ligands, as expected, but its 1:1 copper complex has two broad bands of absorption with maxima at 775 and 800 mμ which were discussed by Jørgensen,[9] who has also commented on the copper complex of EDTA, among other ligands. This author has proposed an empirical parameter equal to the ratio between the observed wave numbers $\bar{\nu}_{Cu}/\bar{\nu}_{Ni}$, which is a measure of the relative tetragonality of the copper complex, because the nickel(II) spectra are very little affected by deviation from cubic symmetry.[8,9] This parameter can be used as a further confirmation for the configurations of the copper complexes considered above.

TABLE II.—DECREASE IN LOG K UNITS FOR METAL COMPLEXES WHEN EDTA IS REPLACED BY EDDMA

	log K EDDPA	log K EDTA	Δ log K
Mg^{2+}	2·8	8·7	5·9
Ca^{2+}	~1	10·7	9·7
Co^{2+}	10·2	16·31	6·1
Ni^{2+}	12·2	18·62	6·4
Cu^{2+}	15·2	18·8	3·6
Zn^{2+}	10·1	16·5	6·4
Cd^{2+}	8·1	16·6	8·5
La^{3+}	5·8	15·4	9·6

There is still another factor favouring ethylenediamine-N,N′-di-α-propionic acid as a reagent for the spectrophotometric determination of copper. It derives from the fact that being a tetradentate ligand, the stability of most of its complexes is much lower than that of the corresponding complexes formed by the above mentioned complexans, but the decrease for copper is far smaller than for the other metals.

Taking EDTA as an example, these conclusions are summarised in Table II.

Relative to EDTA the decrease in stability for the copper complex is about 1,000 times smaller than for other metals. This is expected to reduce considerably the interferences, because the formation of the copper complex becomes preferential in relation to most, if not all the common metals. The study of the interfering elements, described below, confirms this hypothesis.

EXPERIMENTAL

Apparatus

A Beckman model B spectrophotometer with 1-cm corex cells was used for absorbance measurements. A Radiometer TTTc 1 pH meter, with a combined electrode GK-2025 was used.

Reagents

Ethylenediamine-N,N′-di-α-*propionic acid.* This reagent was prepared by condensation of ethylenediamine with α-chloropropionic acid in an alkaline medium, following the instructions of Irving, Shelton and Evans.[6] A white product, melting with decomposition at 278–280° (*lit.* 260–265°), was obtained in 60% yield.

0·01M and 0·1M solutions of the monosodium salt of the reagent were prepared by dissolving the calculated amount of the acid in a solution containing the corresponding amount of sodium hydroxide.

Copper. Electrolytic copper was dissolved in AnalaR nitric acid, the excess acid evaporated and the solution diluted to the required volume.

Other reagents. Sodium hydroxide, nitric acid, sulphuric acid, sodium and other metal salts for the study of the interferences were all of analytical grade.

The polyaminocarboxylic acids used for comparison were either commercial products or were previously synthesised in our laboratory.

Procedure

The following procedure is recommended for general application and especially for the analysis of alloys.

Dissolve 0·1000–0·5000 g of the sample (for percentages of copper between 100% and 10%) with 20 ml of dilute nitric acid (1:2). Expel nitrogen oxides, transfer to a volumetric flask and dilute to 100 ml with distilled water. Pipette 5·0 ml of the solution to a small beaker, add 2·5 ml of 0·1M EDDPA (sodium salt) and adjust to pH 3–9 if necessary. Transfer the solution to a volumetric flask and dilute to 25 ml. Check the pH. Read the absorbance with a spectrophotometer at $\lambda = 670$ mμ. Calculate the percentage of copper in a calibration curve obtained from electrolytic copper using the same technique.

STUDY OF THE ANALYTICAL PROCEDURE

Influence of external variables in formation of copper-EDDPA complex

Colour. The reaction of copper with ethylenediamine-N,N′-di-α-propionate is practically instantaneous. The complex has a deep blue colour ($\lambda_{\max} = 670$ mμ) (Fig. 1) which is stable for several days.

pH. The influence of pH is shown in Fig. 2.

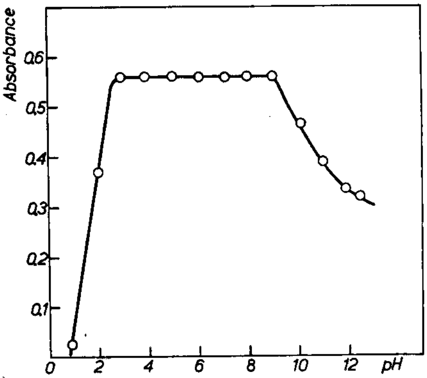


FIG. 2.—Variation of absorbance with pH for the copper-EDDPA complex (concentration of copper 0·004M; concentration of ligand 0·008M).

Below pH 3 the formation of the complex is incomplete and above pH 9 its hydrolysis causes the absorbance to decrease. Between pH 3 and 9 the concentration of the absorbing species is constant and, for analytical purposes, any value of pH between these limits is suitable.

Temperature. A temperature between 10° and 50° has no appreciable effect on the extinction coefficient of the complex.

Ionic strength. The effect of the ionic strength was studied using a 30% solution of potassium nitrate as the upper limit of concentration. The differences in absorbance do not exceed 0·005 unit for the extremes and the solubility of the complex is not affected.

Reagent concentration. The molar ratio method[10] was used to determine the stoichiometry of the complex (Fig. 3). This curve shows that the complex is formed in equimolar proportions of metal and ligand, as expected. A 100% excess of the reagent ensures that the absorbance is constant and larger amounts of ligand can be present without interfering.

Compliance with Beer's law

Beer's law is obeyed up to concentrations of the order of 400 ppm of copper. The calibration curve passes through the origin and the sensitivity is such that 100 ppm of copper gives rise to an absorbance of 0·22. The lower limit of applicability of the method is about 5 ppm of copper, which is a considerable improvement over similar methods.

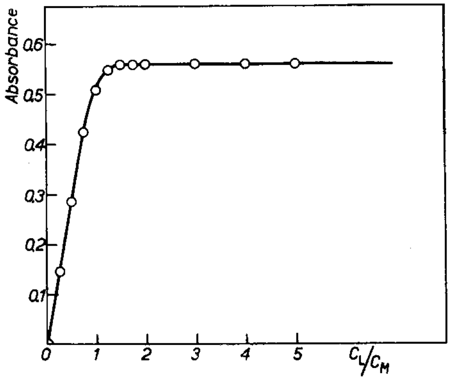


FIG. 3.—Composition of the copper-EDDPA complex (concentration of copper 0·004*M*; pH 6).

Interferences

The effect of foreign cations and anions was studied by adding them to 6 mg of copper and developing the colour with the reagent.

The results obtained showed that sulphates and nitrates do not interfere. Halides may be present up to concentrations 25 times that of copper (chloride and bromide gave errors of +5% when 1 g of NaCl or NaBr was added). Acetate and phosphate can be tolerated in amounts up to about 10 times that of copper; errors of about −4% were obtained when 20 times this amount was used.

Alkali and alkaline-earth ions, manganese, iron, aluminium, zinc, lead, uranium, cadmium, bismuth, chromate, vanadate and molybdate can be considered as non-interfering. Cerium and cobalt can be tolerated in concentrations of the order of, respectively, 10 times and 5 times that of copper. Nickel starts to interfere when present in amounts of the same order of magnitude as that of copper. This metal is practically the only interference which needs to be considered in routine analysis and must be separated when its concentration exceeds that of copper.

RESULTS

We have applied this method to several copper alloys of different compositions, previously analysed by electrolytic deposition in official laboratories. The results obtained are summarised in Table III.

The agreement can be considered as excellent, and deviations may be expected to be less than −0·3% depending on the percentage of copper.

TABLE III.—RESULTS OF ANALYSES OF COPPER ALLOYS[a]

Sample ref.	Copper found, %		Error, %
	Electrolysis	Present method	
L.A. 387	92·14	92·04	−0·11
L.A. 543	67·67	67·50	−0·25
L.A. 544	13·17	13·13	−0·30
L.A. 549	67·68	67·50	−0·25
L.A. 584	99·98	99·90	−0·08
B.C.S. *Bronze* A	85·50	85·45	−0·06

[a] L. A. Laboratório de Análises do Instituto Superior Técnico, Lisbon.
B.C.S. British Chemical Standard.

This makes the present method a very attractive alternative to electrolytic depositions, which are time consuming and have their own difficulties. The spectrophotometric determination of copper using ethylenediamine-N,N′-di-α-propionic acid should be considered when a rapid, easy and considerably accurate method is required for routine determination of this element.

Zusammenfassung—Eine neue Methode zur kolorimetrischen Kupferbestimmung mit Komplexonen wird angegeban. Als Ligand wurde Äthylendiamin-N,N′-di-α-propionsäure (EDDPA) ausgewählt; dieser bietet Vorteile vor allen bisher vorgeschlagenen Komplexonen hinsichtlich Empfindlichkeit und Selektivität. Der Kupferkomplex EDDPA absorbiert bei $\lambda_{max} = 670$ mμ mit $\varepsilon_{max} = 140$ bei allen pH-Werten zwischen 3 und 8. Das Beersche Gesetz gilt bei 0–400 μg Cu^{2+}/ml, und Temperatur oder Ionenstärke tun der Methode keinen Abtrag. Nickel stört, wenn es in der gleichen oder größeren Menge als Kupfer vorhanden ist.

Résumé—On décrit une nouvelle méthode spectrophotométrique de dosage du cuivre avec l'acide ethylènediamine-NN′-di-α-propionique (EDDPA). Le complexe de cuivre présente un maximum d'absorption à $\lambda = 670$ mμ et un coefficient d'extinction molaire $\varepsilon = 140$ dans une zone de pH entre 3 et 8. La loi de Beer est vérifiée pour les concentrations de 0–400 μg Cu^{2+}/ml, la méthode étant plus sensible que les autres méthodes utilisant des complexones proposées jusqu'à présent. La temperature et la force ionique ne gênent pas. Seule l'onterférence du nickel est importante quand ce cation est présent dans des quantités supérieures à celle du cuivre.

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CONTRIBUTIONS TO THE BASIC PROBLEMS OF COMPLEXOMETRY—XIX*

DETERMINATION OF ZINC AND CADMIUM: β-MERCAPTOPROPIONIC ACID AS A MASKING REAGENT FOR CADMIUM

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Summary—A new method for the successive determination of zinc and cadmium (in the presence of copper) is described. It is based on the masking of cadmium (copper) with β-mercaptopropionic acid (MPA) and followed by direct titration of zinc with triethylenetetraminehexa-acetic acid (TTHA). After the addition of DCTA cadmium is determined indirectly by back-titration with zinc nitrate solution. All titrations are carried out with Xylenol Orange as indicator in a slightly acid medium, where alkaline earth metals are without effect on the results.

RECENTLY Yamaguchi and Ueno[1] published some observations on the masking properties of β-mercaptopropionic acid (MPA). In an alkaline medium MPA satisfactorily masks iron, bismuth, cobalt, copper and mercury as colourless or slightly coloured complexes. This masking effect has been used in the complexometric determination of manganese, nickel, calcium, and magnesium in the presence of the above-mentioned metals. MPA has also been used by Hara[2] for masking lead in the EDTA titration of zinc with dithizone as indicator. In an acid medium, however, other complexes are not stable enough to prevent reaction with EDTA.[1] We have confirmed this statement and we have found some interesting reactions of zinc and cadmium, which can be summarised as follows:

(*a*) Cadmium, at pH 5 (urotropine), is masked with MPA against Xylenol Orange. At higher concentrations of cadmium, a white precipitate appears. Zinc does not appear to react with MPA; the zinc colouration with Xylenol Orange still remains even in the presence of excessive MPA.

(*b*) The titration of zinc with EDTA after previous masking of cadmium always gives high results, because the cadmium-MPA complex is not stable enough to mask the cadmium completely. The end-point is, therefore, indistinct.

(*c*) The masking is effective if triethylenetetraminehexa-acetic acid (TTHA)[3] is used as a titrant. Good results for zinc are obtained if the zinc:cadmium ratio does not exceed 1:40.

(*d*) The cadmium-MPA complex (even if it is present as a precipitate) reacts quantitatively with an excess of EDTA. If the excess EDTA is back-titrated with zinc solution, cadmium is displaced to its MPA complex, but the end-point is sluggish and indistinct. (log $K_{CdY} = 16{\cdot}46$ and log $K_{ZnY} = 16{\cdot}50$).

(*e*) DCTA also reacts quantitatively with the cadmium-MPA complex, but the

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* Part XVIII: *Talanta*, 1965, **12**, 385.

cadmium is not displaced by back-titration with zinc (log $K_{\mathrm{CdY}} = 19{\cdot}23$, and log $K_{\mathrm{ZnY}} = 18{\cdot}67$). The end-point of the titration can be located easily. For these reasons DCTA has been used for the determination of cadmium.

(*f*) The colourless copper(I)-MPA complex does not react with either EDTA or DCTA under the same conditions. Therefore, MPA has also been used for the masking of copper in the determination of zinc and cadmium.

Table I.—Determination of cadmium and zinc in the presence of copper

Taken, *ml of 0·05M*			MPA, *drops*	0·05*M* TTHA, *ml*	0·05*M* DCTA, *ml*	0·05*M* Zn, *ml*	Found, *ml of 0·05M*	
Cd	Zn	Cu					Cd	Zn
0·50	10·00	—	25	5·00	1·96	1·58	0·38	10·00
3·01	3·00	—	25	1·48	4·90	1·93	2·97	2·96
5·01	0·50	—	30	0·22	9·81	4·85	4·96	0·44
10·03	0·50	—	30	0·24	11·76	1·87	9·89	0·48
0·50	20·00	—	30	9·92	1·96	1·50	0·46	19·84
0·50	20·00	—	15[a]	10·08	1·96	1·70	0·26	20·16
5·01	10·00	10	25	4·99	9·81	4·85	4·96	9·98
0·50	10·00	10	25	5·01	2·94	2·52	0·42	10·02
5·01	0·50	10	25	0·23	9·81	4·83	4·98	0·46

[a] because of high concentration of zinc the used amount of MPA was not sufficient.

EXPERIMENTAL

Reagents

Triethylenetetraminehexa-acetic acid. 0·05*M* solution of TTHA was prepared by dissolving 24·723 g of the free acid (J. R. Geigy, Basel, Switzerland) in 100–120 ml of 1*M* sodium hydroxide with slight warming and diluting to 1 litre. The factor was checked by complexometric titration with standard 0·05*M* zinc solution with Xylenol Orange as indicator.

β-Mercaptopropionic acid. A commercially available sample (Dojindo, Pharmaceutical Laboratories Kumamoto, Japan) was used without purification and dilution.

Other reagents include 0·05*M* DCTA, and the nitrates of copper, zinc and cadmium, concentrated nitric acid, 1*M* nitric acid, solid urotropine and a 0·2% solution of Xylenol Orange.

Procedures

Successive determination of zinc and cadmium. To the acid solution, containing not more than 40 mg of cadmium and 60 mg of zinc, add 10–40 drops of concentrated MPA, adjust the pH to 5–5·5 with solid urotropine, add Xylenol Orange and titrate slowly with 0·05*M* TTHA to a red-yellow colour. Because TTHA forms a 2:1 complex with zinc,[3] 1 ml of 0·05*M* TTHA corresponds to 6·537 mg of zinc.

To the same solution add an excess of 0·05*M* DCTA and titrate with 0·05*M* zinc nitrate to the red colour of the indicator. One ml of 0·05*M* DCTA corresponds to 5·6205 mg of cadmium.

*Determination of zinc and cadmium in the presence of copper.** To the acid solution, containing up to 40 mg of copper, in addition to the cadmium and zinc, add dropwise MPA to discolouration (a slight turbidity always appears if cadmium is present), and some drops of MPA in excess (1·5 ml of concentrated MPA is the maximum) and determine zinc and cadmium as described above. Some results are given in Table I.

Although thiourea is well known as a very active and selective masking agent for copper, it cannot be used. The addition of MPA to a solution containing the copper-thiourea complex and zinc and cadmium causes a white precipitate which reacts slowly with TTHA and so the results are not good.

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* After we had finished this study, Makada, Yamaguchi and Ueno[4] published a note on dimercaptosuccinic acid, which can also be used as a masking agent for cadmium (copper) in the titration of zinc with EDTA, but only for a ratio of zinc:cadmium of less than 1:1.

DISCUSSION

Although the described method is very simple and gives good results under proper conditions, the reaction mechanism during the second titration is rather complicated. At the first end-point (determination of zinc) $Zn_2(TTHA)$ and Cd(MPA) complexes exist. After the addition of DCTA cadmium is complexed and $Zn_2(TTHA)$ can react partly with DCTA:

$$\mathrm{Zn_2(TTHA) + 2DCTA \rightarrow 2Zn(DCTA) + TTHA} \quad (1)$$

It is impossible to calculate the extent of this reaction by back-titration with zinc, because the consumption of zinc is always the same:

$$\mathrm{2DCTA + 2Zn \rightarrow 2Zn(DCTA)} \quad (2)$$

$$\mathrm{TTHA + 2Zn \rightarrow Zn_2(TTHA)} \quad (3)$$

Reaction (1) can, however, be easily followed by back-titration with lanthanum, which forms only 1:1 complexes with both titrants. Two examples illustrate the solution of this problem.

(*a*) 10 ml of 0·05*M* zinc solution were determined by titration with 5·11 ml of 0·05*M* TTHA. After the addition of 10 ml of 0·05*M* DCTA the solution was titrated again with 0·05*M* lanthanum solution; the consumption was 8·43 ml (instead of 10 ml).

(*b*) The first experiment was repeated and after the addition of DCTA the solution was titrated in the same way after standing for 1 hr. The consumption of 0·05*M* lanthanum solution was only 5·7 ml.

Because reaction (1) is incomplete and x ml of DCTA replace $\frac{x}{2}$ ml of TTHA, the total consumption of lanthanum (A) is given by the following equation:

$$A = 10 - x + \frac{x}{2}.$$

When $A = 8{\cdot}43, x = 3{\cdot}14$ and when $A = 5{\cdot}7, x = 8{\cdot}6$; then the free DCTA $= 10 - x$ ml and liberated TTHA $= \frac{x}{2}$ ml.

In the first experiment the solution contains 6·86 ml of DCTA and 1·57 ml of TTHA; in the second one 1·4 ml of DCTA and 4·3 ml of TTHA. These experiments show that reaction (1) proceeds slowly and is not quantitative even after 1 hr.

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Zusammenfassung—Eine neue Methode zur Bestimmung von Zink und Cadmium nacheinander (auch in Gegenwart von Kupfer) wurde beschrieben. Sie beruht auf der Maskierung von Cadmium (Kupfer) mit β-Mercaptopropionsäure (MPA) und nachfolgende direkte Titration von Zink mit TTHA. Nach Zugabe von DCTA wird Cadmium indirekt durch Rücktitration mit Zinknitrat bestimmt. Alle Titrationen werden mit Xylenolorange als Indikator in schwach saurem Medium ausgeführt, wo Erdalkalien ohne Einfluß auf die Ergebnisse bleiben.

Résumé—On décrit une nouvelle méthode permettant les dosages successifs du zinc et du cadmium (également en présence de cuivre). Elle est basée sur la dissimulation du cadmium (cuivre) au moyen d'acide β mercaptopropionique (MPA), suivie du dosage direct du zinc au TTHA. Après addition de DCTA, le cadmium est dosé indirectement par titrage en retour au moyen d'une solution de nitrate

de zinc. Tous les dosages sont menés en présence de Xylénol Orangé comme indicateur, en milieu légèrement acide, où les alcalino-terreux sont sans influence sur les résultats.

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BEHAVIOUR OF SILVER(II) IN PHOSPHORIC ACID MEDIA AND A GENERAL MECHANISM FOR SOLVENT OXIDATION

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Summary—A spectrophotometric investigation of silver(II) in phosphoric acid solution has revealed the presence of two predominant silver(II) phosphate complexes, which undergo reduction by water according to a rate law second order in silver(II), inverse first order in silver(I) and complex in solvent anion and hydrogen ion concentrations. A comparison of trends in molar absorptivities and pseudo-first order rate constants indicates that the reduction step is preceded by rapid equilibria involving silver(II) complexes. A single oxidation-reduction mechanism seems to be common to the three acidic media studied to date.

BECAUSE silver(II) is a strong oxidising agent in aqueous solution and promises to be useful as a selective oxidant in several stoichiometric reactions of analytical interest, we have previously reported on the nature and stability of this reagent in acidic sulphate[1] and perchlorate[2] media. In our earlier papers we emphasised the importance of silver(II)-solvent ligand complexes and the role of kinetic factors in determining the lifetime of silver(II) with regard to its reduction by water.

In the meantime, Lloyd and Pickering have reported[3] their observations on the use of silver(II) in aqueous solution for the analytical oxidation of manganese(II) and chromium(III). These authors also recognised that the silver(II)-water reaction was responsible for the observed deviations from stoichiometry of the desired oxidation-reduction reaction, and pointed out the need for additional kinetic and mechanistic data in these systems.

The present paper describes our findings regarding the behaviour of silver(II) in phosphoric acid solutions, and thus completes the series of studies employing media of mono-, di-, and tri-basic ligands. On the basis of the equilibrium and kinetic evidence obtained, an attempt is made to arrive at a general reaction scheme for the reduction of silver(II) by water in such solvents and some conclusions are drawn about the use of silver(II) as an effective oxidant for analytical purposes.

EXPERIMENTAL

The reagents, apparatus and procedures used were as described previously.[1]

RESULTS AND DISCUSSION

Previous studies[2,4] have amply demonstrated that the rate of reduction of silver(II) by water is second order in silver(II) and inverse first order in silver(I). This point was confirmed in the present study for this reaction in phosphoric acid media; for purposes of comparison, however, all rate constants are reported as pseudo-first order rate constants and were obtained from rates measured during the early portion of the reaction where the inhibiting effect of silver(I) is minimal.

Spectra of silver(II) as a function of phosphoric acid concentration

Ultraviolet and visible spectra recorded from solutions $4{\cdot}04 \times 10^{-2}$ and $9{\cdot}70 \times 10^{-3}M$ in silver(II) suggest, on the basis of the large rise in absorbance in the ultraviolet region of the spectrum with increasing concentration of phosphoric acid, that at least two phosphate complexes of silver(II) are present in important concentrations in the range of 4 to 44·4*N* phosphoric acid. These predominant species have their absorption maxima at approximately 498 (visible complex) and 300 mμ (ultraviolet complex), respectively. Contary to our findings in sulphuric acid solutions,[1] no reproducible isosbestic point could be distinguished. Small shifts in the location of the maxima occur in changing acid concentrations and can probably be attributed to variable decomposition rates. The spectrophotometric data are summarised in Table I.

Table I.—Spectrophotometric data for silver(II) phosphate complexes as a function of phosphoric acid concentration

H_3PO_4, *N*	Visible complex maximum, mμ	Absorbance	Ultraviolet complex maximum, mμ	Absorbance
44·4	500	0·040	306	0·773
40	498	0·061	301	0·883
38	498	0·067	300	1·063
35	495	0·067	300	1·178
30	495	0·065	300	1·084
25	496	0·031	300	0·331
14	500	0·024	296	0·173
4	500	0·037	280	0·058

Because of the simultaneous disappearance of silver(II) by a reduction process whose rate depends in a complex fashion on both silver and acid concentrations, the data in Table I, while reasonably reproducible, do not give direct information regarding the complexes involved. For this reason, log absorbance *vs.* time curves for each case were constructed and extrapolated to zero time to give the initial molar absorptivities listed in Table II.

Table II.—Molar absorptivity of silver(II) as a function of solution composition

H_3PO_4 medium, *N*	Wavelength, mμ	Molar absorptivity
40	500	25·1 ± 3
35	496	21·2 ± 3
30	496	24·6 ± 3
20	496	18·4 ± 3

Similar experiments carried out under conditions of varying acidity at constant phosphate concentration and varying phosphate concentrations at constant acidity, respectively, yielded the apparent molar absorptivities of Table III.

While there is considerable uncertainty in the actual numerical values given, it can be seen that the calculated molar absorptivities vary roughly in a manner proportional to the square of the phosphate concentration and the inverse square of the hydrogen ion concentration. Analogous experiments carried out for the ultraviolet complex

TABLE III.—MOLAR ABSORPTIVITIES AS FUNCTION OF ACIDITY AND PHOSPHATE CONCENTRATION

Formal H^+ conc.	$\frac{1}{[H^+]^2} \times 10^3$	Formal PO_4^{3-} conc.	$[PO_4^{3-}]^2$	Wavelength, $m\mu$	Molar absorptivity
21·0	22	22·0	—	496	18 ± 3
20·0	25	22·0	—	496	31 ± 3
19·5	26	22·0	—	496	36 ± 3
19·0	28	22·0	—	496	41 ± 3
20·0	—	23·0	530	496	34 ± 3
20·0	—	22·5	505	496	32 ± 3
20·0	—	22·0	485	496	31 ± 3

(at 300 mμ) are less clear-cut, because of the poor reproducibility and optical interference of silver(I) species, but seem to indicate a decrease in the apparent molar absorptivity with increasing phosphate concentration.

Reduction kinetics of silver(II) phosphate complexes

The decomposition of silver(II) phosphate complexes obtained by dissolution of $4{\cdot}04 \times 10^{-2}$ and $8{\cdot}07 \times 10^{-2}M$ silver oxide (AgO) in 40, 35, 30 and 20*N* phosphoric acid was studied at 496 and 300 mμ. The resulting pseudo-first order rate constants (for experiments carried out in triplicate at 25·0 ± 0·15°) are reported in Table IV as a function of phosphoric acid concentration.

TABLE IV.—RATE CONSTANTS FOR SILVER(II) REDUCTION IN PHOSPHORIC ACID

H_3PO_4, *N*	Wavelength, $m\mu$	k, min^{-1}	Wavelength, $m\mu$	k, min^{-1}
40	496	0·097	300	0·092
	496	0·101	300	0·098
	496	0·099	300	0·091
35	496	0·110	300	0·111
	496	0·108	300	0·115
30	496	0·120	300	0·129
	496	0·119	300	0·132
	496	0·120	300	0·125
20	496	0·161	300	0·185
	496	0·188	300	0·185

An important observation immediately becomes apparent: while the specific rate constants show a small increase with decreasing phosphoric acid concentration, the average rate constants obtained for the decomposition of the "visible" and "ultraviolet" complexes are equal at any given phosphoric acid concentration. In fact, the ratio of rate constants obtained in 16 separate experiments was 0·996 ± 0·018.

In view of this rather remarkable finding, our experiments were extended to the entire accessible range of phosphoric acid concentrations (4 to 44·4*N*). Again, the absolute numerical values of the rate constants were constant within about ±15% (relative), and the ratio of the "visible" to the "ultraviolet" rate constant averages 1·036 ± 0·026 for 35 experiments. From experiments carried out over the temperature range 10–40°, an Arrhenius activation energy of approximately 11·5 kcal/mole was calculated.

Finally, the individual effects of hydrogen ion and phosphate concentrations on the rate constant were evaluated in a manner similar to that used above for the measurement of the molar absorptivities. The results of this study are summarised in Table V.

While it was not possible to hold the ionic strength constant in all experiments, the results of Table V clearly show a second order dependence of the rate constant on hydrogen ion concentration and an inverse second order dependence on phosphate concentration. It is particularly noteworthy that this variation is exactly opposite to that noted for the dependence of the molar absorptivity of silver(II) upon these same variables.

Table V.—Variation in pseudo-first order rate constant with hydrogen ion and phosphate concentrations (496 $m\mu$)

Formal H^+ conc.	Formal PO_4^{3-} conc.	k, *min*$^{-1}$
19·0	22·0	0·103
21·0	22·0	0·128
22·0	22·0	0·138
20·0	21·0	0·157
20·0	22·0	0·145
20·0	22·5	0·136
20·0	23·0	0·127

General mechanism for silver(II) reduction in mineral acid media

Four rather striking similarities stand out in the observed kinetics of silver(II) decomposition in all three (perchloric, sulphuric and phosphoric) acid media:

(1) The rate law shows second order dependence on silver(II) and inverse first order dependence on silver(I) concentration.

(2) Arrhenius activation energies are identical (about 11 kcal/mole) in the three media within experimental accuracy.

(3) The rate constants for the decomposition of individual silver(II) complexes in each medium are in a constant 1 : 1 ratio over very wide ranges of solution composition.

(4) Measured rate constants taken under similar conditions of temperature and ionic strength are comparable from one medium to another.

These four observations are consistent with the view that a critical reaction step prevails, which is independent of the nature and charge of the solvent ligand and has general validity for the decomposition of silver(II) in strong acid media. This step is believed to be the disproportionation of silver(II), *i.e.*,

$$2Ag(II) \rightleftharpoons Ag(III) + Ag(I) \tag{1}$$

followed by the reaction of silver(III) with the solvent to yield oxygen and silver(I) as final products.

Nevertheless, the solvent anion has a very definite effect on the over-all sequence of processes in each medium. Most probably, these anions serve as ligands to form a series of silver(II) complexes which are in rapid equilibrium to furnish reactive silver(II) for step (1). That these equilibria must be rapidly established is shown by the absence of rate constant differences when the kinetics of the oxidation-reduction reaction are followed by monitoring the concentration of the individual complexes. It seems likely that considerable analytical advantage is to be gained by proper choice of ligands both for the purpose of stabilising silver(II) in solution and for improving detection limits [*e.g.*, the molar absorptivity of silver(II) is about 1000 times greater in sulphuric acid than in perchloric or phosphoric acid media].

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Zusammenfassung—Eine spektralphotometrische Untersuchung von Silber(II) in phosphorsaurer Lösung ergab die vorherrschende Gegenwart zweier Silber(II)-phosphatkomplexe, die durch Wasser nach einem Geschwindigkeitsgesetz zweiter Ordnung bezüglich Silber(II) und reziproker erster Ordnung bezüglich Silber(I) reduziert werden; die Anionen- und Wasserstoffionenkonzentration tritt in komplizierter Form auf. Ein Vergleich der Änderungen der molaren Extinktionskoeffizienten und der Geschwindigkeitskonstanten pseudo-erster Ordnung zeigt, daß dem Reduktionsschritt rasche Gleichgewichtsreaktionen der Silber(II)-Komplexe vorgelagert sind. In den bisher untersuchten sauren Medien scheint ein und derselbe Oxydations-Reduktionsmechanismus abzulaufen.

Résumé—Une étude spectrophotométrique de l'argent(II) en solution dans l'acide phosphorique a révélé la présence essentielle de deux complexes de phosphate d'argent(II), qui subissent la réduction par l'eau selon une loi de vitesse de second ordre par rapport à l'argent(II), inversement d'ordre un par rapport à l'argent(I), et complexe par rapport aux concentrations du solvant en anion et ion hydrogène. Une comparaison des tendances dans les absorptions molaires et les constantes de vitesse d'ordre pseudo-un indique que le stade de réduction est précédé par des équilibres rapides mettant en jeu des complexes de l'argent(II). Un seul mécanisme d'oxydo-réduction semble commun aux trois milieux acides étudiés jusqu'à présent.

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POTENTIOMETRIC DETERMINATION OF *N*-SUBSTITUTED DITHIOCARBAMATES

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Summary—A simple and general method for the determination of *N*-substituted dithiocarbamates is described. The sample, dissolved in water, is decomposed with a known amount of acid and the solution is back-titrated with standard base. The number of equivalents of dithiocarbamate (as CS_2^- groups) is easily found from the titration curves.

In the course of our studies on properties and analytical application of different amino-*N*-carbodithioates[1–5] (*N*-substituted dithiocarbamates, $R_2N\text{-}CS_2^-$) we have stated the lack of a simple and general method of assaying amino-*N*-carbodithioates. Several methods of determination of amino-N-carbodithioates[6] have been recommended. A commonly used procedure is based on acid digestion of the sample, followed by colorimetric,[7] iodometric[8,9] or other titrimetric[10] determination of the carbon disulphide formed. This seems to be a general method, but it is neither simple nor rapid. A modification of these methods was described by Shankaranarayana and Patel,[11] who add a known amount of standard acid to the carefully neutralised sample and, after decomposition of diethylamine-*N*-carbodithioate, back-titrate the excess of acid with standard sodium hydroxide. Direct iodometric titration of amino-*N*-carbodithioate[12] may be promising, but for some derivatives the end-point is not distinct. Physico-chemical methods have been also used for determination of amino-*N*-carbodithioates, *e.g.*, polarography,[13–15] ultraviolet[16] and infrared[17] spectrophotometry. Their chief disadvantage is connected with the need of standardisation with samples of known composition. Papers employing the formation of coloured chelates of amino-*N*-carbodithioates are of little value until their properties have been thoroughly investigated.

In this study we present a potentiometric procedure in which the sample is hydrolysed with acid. The excess acid and the protonated base, formed by the hydrolysis, is titrated with sodium hydroxide and the titration curve used to interpret the results.

EXPERIMENTAL

Apparatus

Direct reading pH-meter. Radiometer pHM 22, equipped with glass and calomel electrodes.

Reagents

Perchloric acid. 0·1*M* Standard solution.

Potassium hydroxide. 0·1*M* Standard solution, free from carbonate.

Amino-N-carbodithioates. Sodium diethylamino-*N*-carbodithioate, sodium morpholine-*N*-carbodithioate, sodium pyrrolidine-*N*-carbodithioate, sodium piperazine-bis-*N*,*N'*-carbodithioate and sodium piperidine-*N*-carbodithioate were prepared according to the procedure given by Gleu and Schwab.[18]

Ammonium diethanolamino-*N*-carbodithioate and ammonium bis-(carboxymethyl)-amino-*N*-carbodithioate were prepared according to a procedure similar to that of Hass and Schwarz.[19]

Procedure. Titrate the aqueous solution (20 ml) of the amino-*N*-carbodithioate, containing not less than 0·25 mequiv (corresponding to the mmole of carbon disulphide) with standard 0·1*M*, perchloric acid until the pH is reduced to 1·5–2·0 and record the titration curve. Heat the solution and evaporate to one third of the volume. Cool and slightly dilute the solution, then titrate with standard 0·1*M* alkali solution up to about pH 11. The content of the amino-*N*-carbodithioate is calculated from the plot of the titration curves, the amount of the amino-*N*-carbodithioate corresponds to the amount of hydrogen ions used for acid decomposition of the sample.

DISCUSSION AND RESULTS

Titration curves

The decomposition of all amino-*N*-carbodithioates in an acid medium proceeds according to the general equation:

$$R_2N{-}CS_2^- + 2H^+ \rightleftharpoons R_2NH_2^+ + CS_2.$$

This reaction is relatively rapid, but the reverse reaction also proceeds easily. Significant differences in the rate of reaction and the optimum are found for different aminoderivatives. In general, without an excess of acid this reaction is not rapid enough for direct titration, although in some cases the end-point break may be noted.

When the acid-decomposed solution of amino-*N*-carbodithioate is titrated with standard alkali, the neutralisation proceeds stepwise. At first the excess of strong acid is titrated, a further step is concerned with neutralisation of the protonised amine, the last pH change corresponds to addition of excess of base. When amino-*N*-carbodithioate salts of weak bases are titrated an additional neutralization takes place.

The position of the titration curves on the pH-axis depends on the stability of the N—C bond towards acids and on the dissociation constants of the amines formed (Table I). The former factor influences the position of the acid titration curve (Figs. 1 and 2), the latter the position of the base titration curve. The shape of the curves and the magnitude of the pH break at the respective equivalence points determine the possibility of their use as the basis for quantitative analysis. In the case of pyrrolidine derivative the situation is especially favourable. Pyrrolidine-*N*-carbodithioate is decomposed only in hot acidic solutions and pyrrolidine is a rather strong base. Therefore, both pH breaks extend to at least four pH units, making possible titration even with visual indicators. Diethylamine and piperidine derivatives react similarly; the former has been determined with phenolphthalein as an indicator.[11] In the case of the morpholine derivative, visual titration is possible but is not recommended. The piperazine derivative causes an extra break in the base-titration curve, a result of two

TABLE I.—DISSOCIATION CONSTANTS OF AMINES FORMED IN AMINO-*N*-CARBODITHIOATE DECOMPOSITION

Amine	pK_1	pK_2
Diethylamine	11·0	
Pyrrolidine	11·2	
Morpholine	8·7	
Piperidine	11·0	
Piperazine	9·8	5·8
Diethanolamine	9·0	
Iminodiacetic acid	9·5	2·7
Ammonia	9·2	

nitrogen atoms of different basicity. A similar badly developed break may be seen in the curve of the iminodiacetic acid derivative at low pH values. For the ammonium salts the initial potential break is small, because the pH value of the initial solution is relatively low (<9). In these cases the base-titration curve may include titration of the ammonium ion.

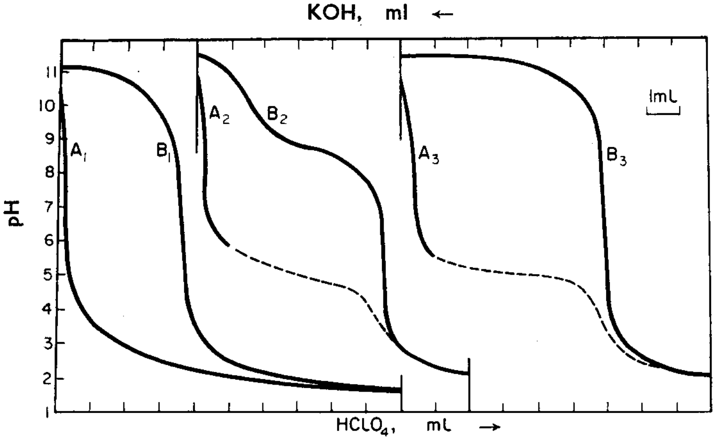

FIG. 1.—Curves of acid, A, and base, B, titration of carbodithioates:
A_1, B_1—sodium pyrrolidine-*N*-carbodithioate
A_2, B_2—sodium morpholine-*N*-carbodithioate
A_3, B_3—sodium diethylamine-*N*-carbodithioate.

Calculations

In quantitative analysis the evaluation of the amino-*N*-carbodithioate assay is based on the potential breaks in both curves. If V_A represents the volume of acid added to the first potential break in the acid titration, corresponding to neutralisation of a small amount of alkali hydroxide added to inhibit the decomposition of the amino-*N*-carbodithioate, V_{AT} the total volume of added acid of concentration C_A,

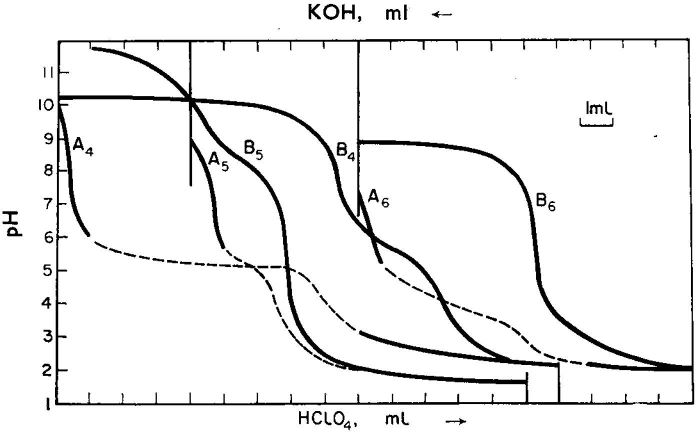

FIG. 2.—Curves of acid, A, and base, B, titration of carbodithioates:
A_4, B_4—disodium piperazine-bis-*N*-carbodithioate)
A_5, B_5—ammonium diethanolamine-*N*-carbodithioate
A_6, B_6—triammonium bis-(carboxymethyl)-amino-*N*-carbodithioate.

and V_B the volume of base of concentration C_B added till the first break in the base titration, then

$$(V_{AT} - V_A) \times C_A - V_B \times C_B$$

represents the amount of equivalents of hydrogen ions used for the decomposition of the sample. Thus, the equivalent of amino-*N*-carbodithioate (1 equivalent corresponds to 1 carbon disulphide group) equals

$$X = \frac{(V_{AT} - V_A) \times C_A - V_B \times C_B}{2}.$$

In the case of piperazine-bis-(*N*-carbodithioate) the calculation may be slightly different, when the point between the two breaks is considered. So the equivalents of hydrogen ions should be divided by 1·5. To improve the accuracy both end-points may be determined and an average result is taken as the basis of the final analysis (Table II). For a very weak amine (pK < 6), the end-point may be taken after the protonised amine has been neutralised. Therefore, the net reaction occurs

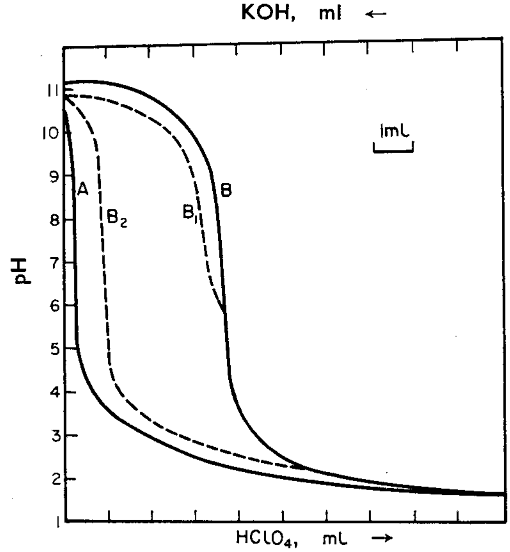

FIG. 3.—Base-titration of various samples of pyrrolidine-*N*-carbodithioate after acid titration, A:

B—sample evaporated to 0·33 volume
B_1—sample heated to boiling
B_2—sample titrated with alkali immediately after addition of acid.

$$R_2N\text{—}CS_2^- + H^+ \rightleftharpoons R_2NH + CS_2$$

and the number of hydrogen equivalents equals the number of amino-*N*-carbodithioate equivalents.

Effect of heating

Prolonged heating of the acidic solution may be necessary for complete decomposition of the sample. Three equal samples of pyrrolidine-*N*-carbodithioate were titrated with acid (Fig. 3). One of them was immediately back-titrated with alkali, the second was heated to boiling and then titrated, the last one was heated and evaporated to 0·33 volume remained before titration was performed. In the first two

TABLE II.—REPRODUCIBILITY OF RESULTS OF DISUBSTITUTED AMINO-*N*-CARBODITHIOATE DETERMINATION

Compound	Mequiv	Av. mequiv
Sodium diethylamine-*N*-carbodithioate	2·91	
	2·95	
	2·96	
	2·96	
	2·98	
	2·93	
	2·93	2·95
Sodium pyrrolidine-*N*-carbodithioate	2·82	
	2·79	
	2·79	
	2·81	2·80
Sodium morpholine-*N*-carbodithioate	2·82	
	2·86	
	2·86	2·84
Sodium piperidine-*N*-carbodithioate	2·24	
	2·25	
	2·31	2·27
Disodium piperazine-bis-(*N*-carbodithioate)*		
I 2·83 II 2·90	2·87	
2·88 2·94	2·91	
2·91 2·93	2·92	2·90
Ammonium diethanolamine-*N*-carbodithioate	2·22	
	2·18	
	2·27	2·22
Triammonium bis-(carboxymethyl)amino-*N*-carbodithioate	2·46	
	2·44	
	2·51	
	2·47	
	2·40	2·46

* Results given for both end-points and finally the mean for both.

TABLE III.—RESULTS OF DETERMINATION OF DIETHYLAMINE-*N*-CARBODITHIOATE FOR SAMPLES OF VARIOUS SIZE

Taken, *mg*	22·3	66·8	111·3
Found, *mg*	22·6	65·5	110·4
	22·1	66·6	112·0
	21·9	66·7	111·1
	23·1	66·7	110·6
	21·2	67·2	111·5
		66·0	
		66·0	
Average	22·2	66·4	111·1
Standard deviation	0·72	0·57	0·66
Coefficient of variation	3·25	0·88	0·59

solutions the results were lower (only about 30% of the taken amount of the first sample was accounted for) and even an additional break was observed, which was significant for samples of various derivatives. The complete decomposition of the sample may be tested by adding copper solution to the final solution. A yellowish or brown colour should not be observed. Correct and reproducible results have been obtained for different carbodithioates (Table II).

Accuracy and precision

The final result of determination is calculated as a difference of two volumes (or number of equivalents). Care is needed to take for the determination a proper amount of the sample, otherwise the small difference of two quantities results in a relatively large error (Table III). A reasonable precision may be attained when about 3 mequiv of carbodithioate, corresponding to 60–70 mg of the sample, is taken for determination.

Acknowledgment—The authors are indebted to Prof. Dr. W. Kemula, the Head of the Department of Inorganic Chemistry, University of Warsaw, for helpful and stimulating comments and discussions.

Zusammenfassung—Eine einfache und allgemein anwendbare Methode zur Bestimmung N-substituierter Dithiocarbamate wird beschrieben. Die in Wasser gelöste Probe wird mit einer bekannten Menge Säure gespalten und die Lösung mit eingestellter Lauge zurücktitriert. Die Anzahl der Dithiocarbamat-Äquivalente (als CS_2^--Gruppen) läßt sich aus den Titrationskurven leicht ermitteln.

Résumé—On décrit une méthode simple et générale de dosage des dithiocarbamates N-substitués. La prise d'essai, dissoute dans l'eau, est décomposée par une quantité connue d'acide, et la solution est dosée en retour par une base titrée. Le nombre d'équivalents de dithiocarbamate (à l'état de groupes CS_2^-) se determine aisément à partir des courbes de titrage.

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A SIMPLE COMPUTER CIRCUIT FOR AUTOMATIC SPECTROPHOTOMETRIC ANALYSIS OF BINARY MIXTURES BY DIFFERENTIAL REACTION RATES

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Summary—A simple analogue computer circuit, for application with a continuous reading spectrophotometer to give automatic analysis of binary mixtures of closely related substances using a differential reaction rate technique, is described. The circuit solves the simultaneous equations of the Method of Proportional Equations for the concentrations of the components in the mixture. The method is useful for first- or pseudo-first order competitive reactions. A timing circuit automatically supplies the absorbance (converted as described from the transmittance) of the reacting solution at two chosen times during the reaction, to the computer. The output voltages are adjusted within the circuit to read directly in units of concentration.

INTRODUCTION

IN recent years several analytical techniques based on differential reaction rates have been devised for the *in situ* simultaneous quantitative determination of mixtures of closely related substances.[1–11] All the techniques devised require a rather laborious graphical[5] or mathematical[1] treatment of the data in order to arrive at the concentrations of the unknowns of interest. This paper describes the circuit of an automatic read-out system for the *Method of Proportional Equations*. It can be attached to virtually any continuous reading spectrophotometer that gives an electrical output signal proportional to the transmittance of the sample solution. The simultaneous equations are solved by a simple analogue computer circuit.

PRINCIPLES OF AUTOMATIC READ-OUT CIRCUIT

The *Method of Proportional Equations* can be used for the simultaneous analysis of mixtures of closely related substances if a reagent R can be made to react under pseudo first order conditions with each of the n components A, B, . . . , N of the mixture at different rates, K_A, K_B, . . . , K_N to form a common product, O, or different products yielding a similar instrument response.

The circuit described in this paper was designed for the analysis of a two component mixture. However, by following the principles given below it can easily be extended to mixtures of more than two components. The reaction product(s) that are formed are assumed to absorb light at the same wavelength (if two products result, the fact that they might have different extinction coefficients at the wavelength used does not effect the validity of the method[1,6]) and to follow Beer's law. The proportional

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[*] Participant in University of Michigan Undergraduate Honours Research Programme.

equations for two unknowns have the form:

$$P_1 = K_{A_1}[A]_0 + K_{B_1}[B]_0 \tag{1}$$

$$P_2 = K_{A_2}[A]_0 + K_{B_2}[B]_0 \tag{2}$$

where P_1 and P_2 are the experimentally measured parameters which are proportional to the absorbance of the reaction mixture at times t_1 and t_2 during the reaction, K_{A_1}, K_{B_1}, K_{A_2}, and K_{B_2} are the proportionality constants, and $[A]_0$ and $[B]_0$ are the initial concentrations of the species to be analysed [see references 1 and 6 for the derivation of equations (1) and (2)].

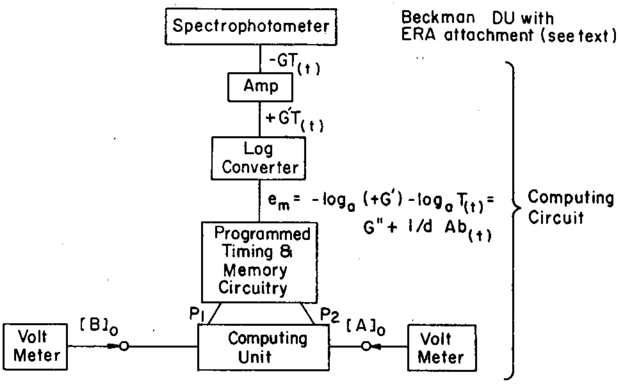

FIG. 1.—Block diagram of automatic read-out apparatus.

A block diagram of the complete analytical system is shown in Fig. 1. The spectrophotometer used in this work was a Beckman DU equipped with a Beckman Energy Recording Adapter (ERA). The ERA converts the phototube current to a voltage suitable for the input of a recorder. [Any recording spectrophotometer can be used with the read-out circuit described, provided that the instrument can be operated at a fixed wavelength. The instrument's output (the input to the spectrophotometer's recorder) is fed directly into the read-out circuit.] The output of the ERA unit, $-GT(t)$, is proportional to the transmission, $T(t)$, of the sample solution at the selected wavelength at any time during the reaction. The proportionality constant is G. Voltages proportional to the absorbance are needed for computation: the logarithm of the output of the ERA must be taken. First, however, the voltage, $-GT(t)$, is fed into a high input impedence amplifier which serves a dual purpose: its high input impedence prevents loading of the ERA output, and it amplifies the original signal $-GT(t)$ to a new signal $+G'T(t)$ which is in the range (1–10 V) for proper operation of the log circuit. By its nature, the amplifier inverts the sign of the input.[12] The device used to perform the logarithmic operation on the input signal was a slightly modified version of the circuit described by Savant and Howard.[13] The response of the circuit was directly logarithmic for the above input voltage range with a 1-V input corresponding to a 0-V output. The output of the log circuit is thus:

$$e_m = -\log_a [G'T(t)] = -\log_a G' - \log_a T(t). = +G'' - \log_a T(t) \tag{3}$$

where G'' is the constant $-\log_a G'$.

The absorbance, $Ab(t)$, of a system is defined in terms of transmission

$$Ab(t) \equiv -\log_{10} T(t) = d \log_a T(t) \tag{4}$$

Substituting equation (4) into (3) gives the output of the log circuit in terms of the absorbance and the constants G'' and $1/d$

$$e_m = +G'' + 1/d\, Ab(t) \tag{5}$$

At two preselected times, t_1 and t_2, during the reaction, a programmed timer feeds the signal e_m into memory units. In the memory units, the sign of e_m is inverted; thus, two voltages $-P_1 - \alpha G''$ and $-P_2 - \alpha G''$ (α is a constant introduced by the memory unit) are available for computation of $[A]_0$ and $[B]_0$ by a simple computer circuit at any time after t_2. For detailed descriptions of the memory and computer circuits see below.

Two operational amplifiers employed as conventional integrating circuits[12,14] were used as the memory units (see Fig. 2). The voltage e_m entering the integrator circuit is of the form in equation (5). At time t_1, the switching circuit applies $e_m(t_1)$ to the integrator for a time Δt_1 that is short in comparison to the reaction time, t_1. The output of the integrator is then:

$$e_{m_1}\,\text{out} = -\frac{1}{RC}\int_{t_1}^{t_1+\Delta t_1} e_m(t)\,dt = -\frac{1}{RC}\int_{t_1}^{t_1+\Delta t_1}\left[G'' + \frac{1}{d}Ab(t)\right]dt \tag{6}$$

Because Δt_1 is short, $e_m(t_1)$ can be considered constant during the interval and to have a value $e_m(t_1)$. (R is the value of the resistance and C the capacitance of the elements of the integrator circuit and e_{m_1} is the output of the memory circuit.) Thus,

$$e_{m_1}\,\text{out} = -\frac{1}{RC}\int_{t_1}^{t_1+\Delta t_1} e_m(t)\,dt = -\frac{1}{RC}[G'' + \frac{1}{d}Ab(t_1)]\Delta t_1 \tag{7}$$

$$= -\frac{\Delta t_1}{RC}G'' - \frac{\Delta t_1}{RC}\frac{Ab}{d}(t_1)$$

$$= -\alpha G'' - \frac{\alpha}{d}Ab(t_1) \tag{8}$$

where α = a constant = $\Delta t_1/RC$. Note that the sign of the voltage of equation (5) has been inverted.[12] At time t_2 the programmed timer feeds the signal $e_m(t_2)$ into the second integrator. By the same arguments as above the signal output of the second memory unit is:

$$e_{m_2}\,\text{out} = -\alpha' G'' - \frac{\alpha'}{d}Ab(t_2) \tag{9}$$

The two integrators hold (as a memory) e_{m_1} out and e_{m_2} out, respectively, after the input signals are applied.[12] If $\Delta t_1 = \Delta t_2$ and the RC constants of the integrators are identical, $\alpha = \alpha'$. The two signals in the memory are:

$$\left.\begin{aligned} e_{m_1}\,\text{out} &= -\alpha G'' - \frac{\alpha}{d}Ab(t_1) = -\alpha G'' - P_1 \\ e_{m_2}\,\text{out} &= -\alpha G'' - \frac{\alpha}{d}Ab(t_2) = -\alpha G'' - P_2 \end{aligned}\right\} \tag{10}$$

The use of integrator circuits for the memories allows a small but finite current to be drawn from them for computing without effecting the values e_{m_1} out and e_{m_2} out.[12]

The voltages in the memory are proportional to the absorbance at t_1 and t_2 [equations (10)] but contain the additive constant potential $-\alpha G''$. At a finite time, 1 min after t_2, the programmed timer then applies e_{m_1} out and e_{m_2} out to the two operational amplifiers of the computing circuit. (See below for a detailed discussion of the timer.) The computing circuit (see Fig. 2) used is a standard analogue circuit for solving a system of simultaneous equations.[11] Simultaneously, the timing circuit applies a voltage equal to $+\alpha G''$ to each amplifier. The circuit is designed so that the $+\alpha G''$ voltage is added to both signals, e_{m_1} out and e_{m_2} out. The result is an effective input to the computer of $-P_1 = \left[-\frac{\alpha}{d}Ab(t_1)\right]$ and $-P_2 = \left[-\frac{\alpha}{d}Ab(t_2)\right]$. These voltages are thus directly proportional to the concentrations of products of the reactions at the times t_1 and t_2, and are exactly the voltages necessary to solve equations (1) and (2) for $[A]_0$ and $[B]_0$. The input and feedback impedences of the computer network are chosen to make the output of the computer read directly in terms of the concentrations of $[A]_0$ and $[B]_0$. No further calculation is necessary. (For a detailed discussion of the computing circuit, see below.) It is a simple matter to connect two voltmeters to read $[A]_0$ and $[B]_0$. Digital voltmeters, such as the Electro Instruments (San Diego, California, U.S.A.) Model 4000 Digital Voltmeter, are recommended to give numerical display of the read-out.

It should be noted that although the above circuit is constructed for a spectrophotometric method of following the reaction, any method that gives an output signal directly proportional to the concentration of product(s) can also be used. In such a case, the logarithmic circuit is omitted and the amplified signal applied directly to the timer-memory circuit.

EXPERIMENTAL

Construction and operation details of each circuit in the automatic read-out system are given below.

Amplifier circuit

This circuit consists of two parts, (i) a standard type high input impedance ($\sim 10^{13}\,\Omega$) voltage follower *F* which prevents loading of the spectrophotometer output,[12] and (ii) a variable gain amplifier (gain of $-$G) which is capable of amplifying the signal by a factor of -1, -10, -10^2 and -10^3. (The sign inversion is inherent in analogue circuits of this type.[14]) These circuits are standard and the details of their operation and associated equipment (power supply, bias, *etc.*) are found in references 12 and 14.

Logarithmic circuit

The logarithmic circuit is essentially the same as that described by Savant and Howard.[13] The 350 Ω and 3·5 K potentiometer are used to bias the tube so that it operates on the logarithmic portion of its characteristic curve for the 1–10 V input range. The 10 K and 250 K potentiometer are then adjusted to make the output read 0 V with a 1-V input. It was found that the rise-time response of this circuit on a 1-V instantaneous change input was about 10 sec. This is well within the time required to follow most reactions for which this technique would be employed,[1,15] but must be considered when the unit is used with fast reactions. Considerable current is drawn from the -6 V bias supply because there is only 350 Ω to ground at this point. If a standard type "C" battery is used, there is a noticeable change in the circuits' characteristics after continuous operation for 6 hr. This can be reduced by using an automobile battery or a commercial transistorised low voltage power supply instead. The ±300 V d.c. operating voltage of the circuit is supplied by the same power supply that runs the operational amplifiers (a Philbrick R-100 B ± 300 V d.c. power supply was used[14]). The adjustable base resistor of this circuit[13] is used to adjust the logarithmic base to a convenient value to give a slope of about 1 on a semi-log plot of output *vs.* input. A value of 10 Meg was used in this work. Other satisfactory logarithmic circuits based on the logarithmic characteristics of certain transistors are described in the literature.[16]

Programmed sequence timing and memory circuit

As stated before, the memory circuits are simply two conventional analogue computer operational amplifiers (Philbrick K2-W, K2-P stabilised units were used[14]) connected as integrators[12,14] (Fig. 2). The two variable resistors R_6 in the integrator circuits are used to equalise the RC time constants of the integrators [see equations (7)–(9)]. The two identical bridge circuits (R_8, R_9, R_{10} and R_{11}) are connected to the summing points[14] of the two integrators. They supply a small current (adjustable by R_{10}) to compensate for leakage in the system (amplifier grid current, capacitor leakage, *etc.*).[12]

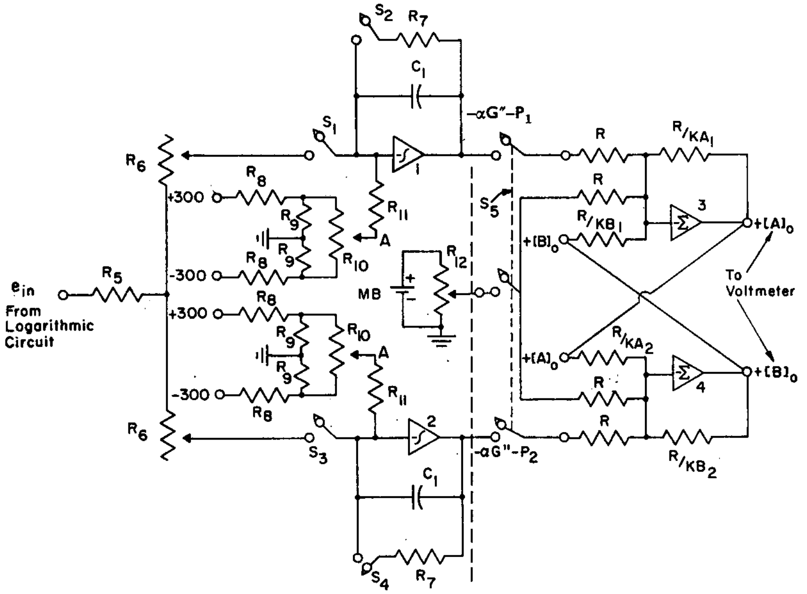

FIG. 2.—Memory and computing circuits:

R = 100 k to 10 Meg (see text)
R_5 = 7 M 1%
R_6 = 1M—Used to equalise RC time constants of integrators
R_7 = 500 Ω
C_1 = 1·0 Mfd
R_8 = 1 M 1%
R_9 = 39 Ω
R_{10} = 500Ω
R_{11} = 10 M
R_{12} = 1K, 2W
MB = Mercury battery of necessary magnitude.

The timing circuit, shown in Figs. 2 and 3, operates as follows: Switches S_8, S_9 and S_{10} are microswitches that are activated by a synchronous timer. S_8 can also be activated by a latching relay (Fig. 3), R built into the timer and controlled by S_6 (this timer is an Industrial Timer Corporation Model RC-8 unit). Closing switch S_6 starts the timer motor by activating S_8. [Note. Fig. 3 shows the circuit just after the cycle has been started and before any signal has been applied to the memory]. S_8 then stays in the position shown in Fig. 3 until the end of the cycle when it automatically opens and stops the motor. At a time t_1 during the reaction, S_9 is closed by the timer cam for a time Δt_1 that is *small* (less than 1 %) compared to the over-all reaction time. This accomplishes two operations: (i) It opens the latching relay S_2 so that the short circuit (discharge path) though R_7 around capacitor C_1 (see Fig. 2) is opened, which permits C_1 to then store a potential [S_2 remains latched in this position for the rest of the cycle until manually reset by closing S_7 momentarily (described later)]. (ii) Simultaneously, S_1, which applies the output of the logarithmic circuit at t_1 into the integrator is closed. It opens again after a time Δt_1 when S_9 opens again (timer activated). Thus $G'' + \frac{1}{d} Ab\,(t_1)$ is applied to, and its integral is stored on, integrator 1. At time t_2, the timer closes S_{10} for a time $\Delta t_2 = \Delta t_1$. Relays S_3 and S_4 operate similarly to S_1 and S_2 in controlling the sequence of events in the second integrator circuit. Then, at any time $t > t_2$, the output of integrator 1 is $-\alpha G'' - P_1$ and the output of integrator 2 is $-\alpha G'' - P_2$. At a time $t > t_2$, dependent on the duration of the timer cycle, the timer automatically turns itself off. Switch S_8 goes to the upper position [position (1)] in Fig. 3. This activates relay S_5. This relay then applies $-\alpha G'' - P_1$, $-\alpha G'' - P_2$ and $+\alpha G''$ into the inputs of the computing circuit [see Fig. 2 and equation (10)]. The computer then develops $[A_0]$ and $[B_0]$ as output voltages and will hold these "answers." (The computing process is described below). To reset the latching relays, S_2, S_4 and S_5, and thus erase the memory in preparation for another run, S_7 is closed momentarily. However, it will be noticed that if S_8 is in the upper position [position (1) in Fig. 3], S_5 will get a signal to activate again. Thus, the proper reset sequence is the following: close S_6 momentarily to activate relay R and thus S_8. The timer motor is now running [S_8 in position (2)]. Immediately close S_7 momentarily to reset S_2, S_4 and S_5. (If it is desired to erase the memories without reactivating the cycle, just close S_7, but recall that S_5 will *not* be reset.)

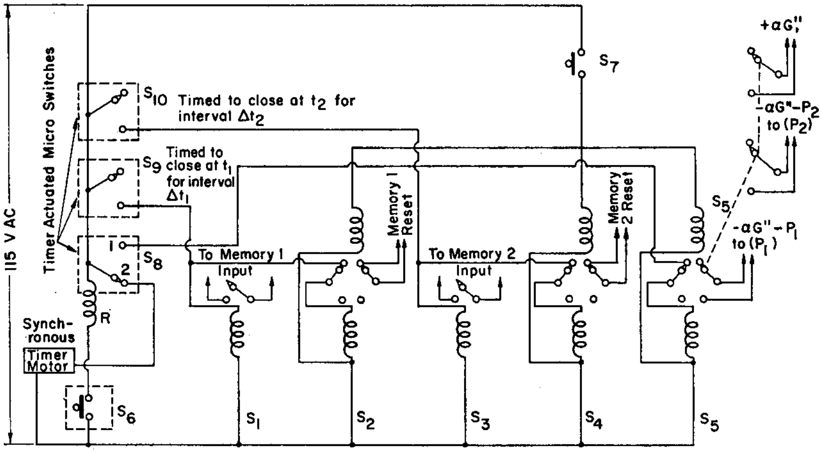

FIG. 3.—Programmed Timing Circuit (controls the sequence of the activation of the switches in the memory and computing circuits; switch numbers are the same as in Fig. 2):

Timer—Industrial Timer Corp., Model RC-8;
S_1 and S_3—Potter-Brumfield Relay—Model #KA11AY 115 V a.c.;
S_2, S_4 + S_5—Potter-Brumfield Latching Relay—Model #KB17AY 115 V a.c., 4PDT.

Switches S_8, S_9 and S_{10} are cam operated and t_1, Δt_1, t_2 and Δt_2 are easily preset to any desired value. The desired duration of the full cycle will depend on the speed of the reaction that is being followed. The length of the timer cycle can be adjusted by simply changing the synchronous motor gear ratios. Different sets of gears are commercially available that can vary the cycle from 10 sec to several hours.

Computing circuit

The computing circuit consists of two summing operational amplifiers[12,14] (Fig. 2). The principles governing the application of summing amplifiers in solving simultaneous equations can be easily shown by rearranging the proportional equations (1) and (2) in the form

$$[A]_0 = \frac{P_1}{K_{A_1}} - \frac{K_{B_1}}{K_{A_1}}[B]_0 \tag{11}$$

$$[B]_0 = \frac{P_2}{K_{B_2}} - \frac{K_{A_2}}{K_{B_2}}[A]_0 \tag{12}$$

The memory circuits have stored the voltages $-\alpha G'' - P_1$ and $-\alpha G'' - P_2$, which can be substituted as input voltages (e_{in_1} and e_{in_2}) along with the voltage $+\alpha G''$ (e_{in_3}) in the expression describing the operation of a summing amplifier[14] (the value of the feedback resistor, R_f, is any convenient value such that all the resistance values fall between 10 K and 20 M). One obtains:

$$\begin{aligned} e_{\mathrm{out}} &= -(-\alpha G'' - P_1)\frac{1}{K_{A_1}} - \alpha G''\frac{1}{K_{A_1}} - (+[B]_0)\frac{K_{B_1}}{K_{A_1}} \\ &= +\frac{P_1}{K_{A_1}} - [B]_0\frac{K_{B_1}}{K_{A_1}} \end{aligned} \tag{13}$$

This is the expression for $+[A]_0$ of equation (11). A similar circuit can be used to calculate $+[B]_0$. [The voltage $+\alpha G''$ is supplied by means of a mercury battery MB which can be varied from 0 to about 20 V and it is adjusted precisely by the potentiometer (10 turn Helipot) R_{12}.] Of course, the values, $+[B]_0$ and $+[A]_0$, which are the solutions sought, are not available as such for substitution into the right hand side of equations (11) and (12). However, if the output of amplifier 3 is fed back into the $+[A]_0$ input of amplifier 4 and the output of 4 fed into the $+[B]_0$ input of amplifier 3, when the potentials $-\alpha G'' - P_1$, $-\alpha G'' - P_2$ and $+\alpha G''$ are applied to the respective inputs (see Fig. 2), the circuit will rapidly come to steady state condition with $+[A]_0$ and $+[B]_0$ reading at the outputs,[1,17] This type of *solution feedback* is the basic principle of all analogue computation.[1,12,14,17]

The values of K_{A_1}, K_{B_1}, K_{A_2} and K_{B_2} are experimentally determined by reacting a solution of pure A and then pure B and measuring P_1 and P_2 for each at times t_1 and t_2. The values of K_{A_1}, *etc.*, are then calculated simply from:

$$\begin{aligned} K_{A_1} &= P_{A_1}/[A]_0 \\ K_{B_1} &= P_{B_1}/[B]_0 \qquad (14) \\ &\vdots \\ &\textit{etc.} \end{aligned}$$

In order to determine the accuracy and precision of the automatic read-out unit, a large number of simulated reaction rate curves were applied to this unit by means of an electronic function generator. These simulated rate curves were constructed from theory using several different cases. (Different rate constants and ratios of $[A]_0/[B]_0$) were used, rather than actual experimental rate curve responses from the spectrophotometer in the evaluation of the automatic unit in order to eliminate all source of variation of parameters not directly introduced by the read-out unit. Thus, no error resulting from spectrophotometer drift, temperature change of the reacting solution, *etc.*, complicated the comparison of the hand calculated and automatic read-out results, and the accuracy and precision of the automatic read-out unit is obtained exactly.) It was found that the results obtained by the automatic read-out unit had an accuracy of better than ±2% when compared with the hand calculated (theoretical) results and a precision (standard deviation) of less than ±2%, when care is taken in measuring the proportionality constants, K's, and in adjusting the instrument.

The increased speed over hand calculation of determining the values of the experimental proportionality constants of the system as well as the analysis result make this unit very useful when large numbers of analyses are being made with this kinetic method. The computing unit would be even more useful when the mixtures contained three or four components because the calculation becomes very tedious in these cases.

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Zusammenfassung—Eine einfache Analogrechnerschaltung wird beschrieben, die mit Hilfe eines kontinuierlich anzeigenden Spektralphotometers eine automatische Analyse binärer Mischungen nahe verwandter Substanzen liefert, wobei eine Technik verwendet wird, die sich auf Reaktionsgeschwindigkeitsunterschiede gründet. Die Schaltung löst die simultanen Gleichungen der Methode der proportionalen Gleichungen für die Konzentrationen der Bestandteile in der Mischung. Die Methode ist von Nutzen bei Konkurrenzreaktionen erster oder pseudoerster Ordnung. Eine Zeitgeberschaltung gibt die Extinktion (die auf bekannte Weise aus der Durchlässigkeit erhalten wird) der reagierenden Lösung zu zwei wählbaren Zeiten während der Reaktion automatisch in den Rechner. Die Ausgangsspannungen werden in der Schaltung so justiert, daß sie direkt Konzentrationseinheiten angeben.

Résumé—On décrit un circuit calculateur analogique simple, en liaison avec un spectrophotomètre à lecture continue, pour l'analyse automatique de mélanges binaires de substances étroitement apparentées, par l'emploi d'une technique de vitesses de réaction différentielles. Le circuit résout les équations simultanées de la méthode des équations proportionnelles, pour les concentrations des composants du mélange. La méthode est utile pour les réactions concurrentes d'ordre un ou

pseudo-un. Un circuit chronométreur fournit automatiquement au calculateur l'absorption (à partir, ainsi qu'il est décrit, de la transmission) de la solution réagissante à deux instants choisis durant la réaction. Les voltages à la sortie sont ajustés dans le circuit de façon à permettre la lecture directement en unités de concentration.

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DETERMINATION OF AMINOALKYLTHIOPHOSPHORUS COMPOUNDS AND THIOLS WITH PALLADIUM(II) IONS AS THE REAGENT

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Summary—Two methods of determination based on the reactions of the palladium(II) ion with thiol compounds, thiocholine esters and thiophosphorus compounds are described. One of the methods is photometric, and the substance measured is the palladium-thiol complex formed when palladium chloride is added to a solution of a thiocholine ester or a thiophosphorus compound. The second method, used for the determination of thiol compounds, is titrimetric, with a palladium chloride solution as the titrant.

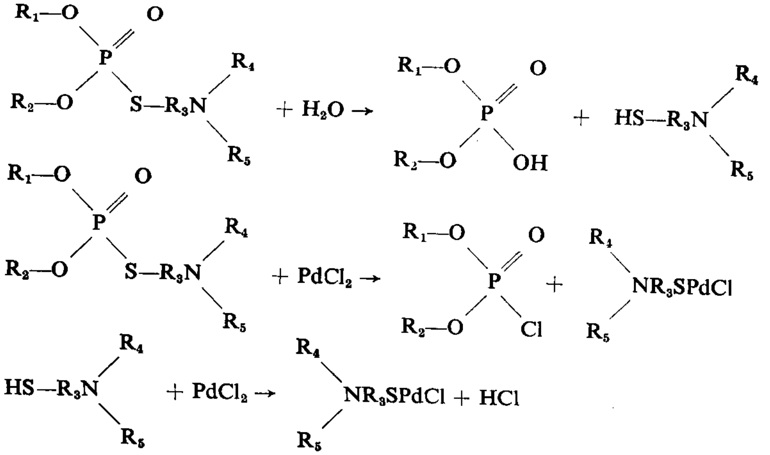
INTRODUCTION

THE many methods available for the determination of thiols, organic sulphides, thiophosphorus compounds and thiocholine esters have been reviewed in detail by Cecil and McPhee[1] and by MacDougall.[2] The latter has used fluorimetric measurements for the determination of pesticide residues. Mercurimetric methods for the determination of thiols, aryltriethyl sulphides and disulphides have been described by Gregg, Bouffard and Barton.[3] Fritz and Palmer[4] have also made mercurimetric determinations of thiols. At this laboratory we were in need of methods for determining the main components and decomposition products of thiocholine esters and aminoalkylthiophosphorus compounds, *e.g.*, dimethylaminoethylthiodiethoxyphosphine oxide and dimethylaminoethanethiol.

PRINCIPLES

Thio compounds of the type shown in equation (1) are almost invariably contaminated by the corresponding thiol compounds formed by hydrolysis. To determine the extent of this contamination two methods have been worked out, both of them based on the reaction of the palladium ion with the two types of compound.

The reactions involved are the following:



(1)

(2)

(3)

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With thiol compounds the palladium ion instantaneously forms stable complexes, which can be written as $PdSR^+$ and $Pd(SR)_2$.

The effect of palladium ions on some thio compounds, *e.g.*, thiocholine esters or aminoalkylthiophosphorus compounds, which can be transformed by hydrolysis to thiol residues, is to increase the rate of decomposition in ethanol or aqueous solutions. After distillation of the reaction products of equation (2), the presence of the phosphoryl chloride may be demonstrated by applying Schönemann's reaction[5] to the distillate. In aqueous solution the phosphoryl chloride is rapidly hydrolysed. The palladium-mercapto chloride formed is a very stable complex, which absorbs radiation in the ultraviolet range.

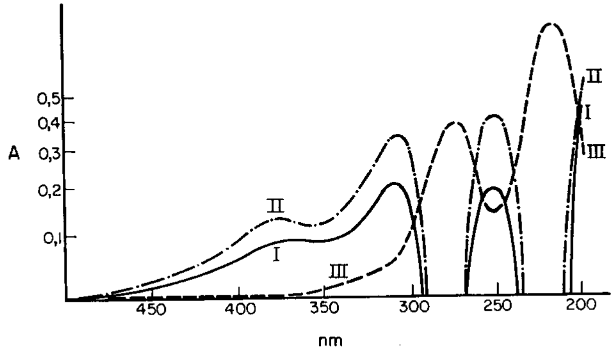

FIG. 1.—Absorbance curves (the substances are dissolved in 0·3*M* hydrochloric acid):

I. Dimethylaminoethylthiodiethoxyphosphine oxide + palladium chloride, measured against a palladium chloride solution.
II. The corresponding dimethylaminoethanethiol + palladium chloride, measured against a palladium chloride solution.
III. Palladium chloride solution measured against 0·3*M* hydrochloric acid.

The palladium–thiol complex can be assayed by photometry in the ultraviolet range and a direct titration of the thiol compound with a palladium chloride solution is possible. At the equivalence point excess palladium is indicated by a colour reagent.

The photometric method has recently been applied in work described by Åkerfeldt and Lövgren.[6]

EXPERIMENTAL

Photometric Method

The absorbance curve from 220 to 500 nm for dimethylaminoethylthiodiethoxyphosphine oxide + palladium chloride in 0·3*M* hydrochloric acid, measured against a reference solution of palladium chloride in 0·3*M* hydrochloric acid, and the corresponding absorbance curve for dimethylaminoethanethiol + palladium chloride are identical (Fig. 1). This confirms the reaction represented by equation (2). The reaction times may vary from minutes to hours, depending on which substances are used.

The absorbance curves have two maxima, at 250 and 310 nm. They also have two minima, at 280 and 225 nm; both are "negative". The absorbance curve for the reference solution, palladium chloride in 0·3*M* hydrochloric acid, measured against 0·3*M* hydrochloric acid, also has two maxima at 280 and 225 nm—the same wavelengths as for the minima for the palladium–thiol complex. The formation of the complex on mixing a thiol compound with the palladium reagent results in a decrease in the palladium ion concentration. For the reagent solution in the reference cell, however, the palladium ion concentration is unchanged, and because it is higher than for the sample, the absorbance is higher at 280 and 225 nm than for the sample solution. This is the reason for the "negative" absorbance at the two minima.

The measurements are carried out in acid solutions with a pH of less than 3. At higher pH the absorbance curve for a palladium chloride solution no longer has well defined peaks at 280 and 225 nm, but two broad maxima at 250 and 225 nm, which merge (Fig. 2). If measured at a pH of more than 3 the maximum of the palladium-thiol complex at 250 nm is disturbed, so that at this wavelength, too, a "negative" absorbance may appear.

Beer's law is obeyed for both absorbance maxima. For 10^{-5}–$10^{-3}M$ solutions the absorptivity at 250 nm is 5×10^{3} and at 310 nm it is 4×10^{3} litre. mole^{-1}. cm^{-1}. The standard deviation for a single value at 250 nm is $4{\cdot}0 \times 10^{-7}$ mole/litre (measured on $7{\cdot}4 \times 10^{-5}$ molar solutions) and at 310 nm it is $10{\cdot}0 \times 10^{-7}$ mole/litre.

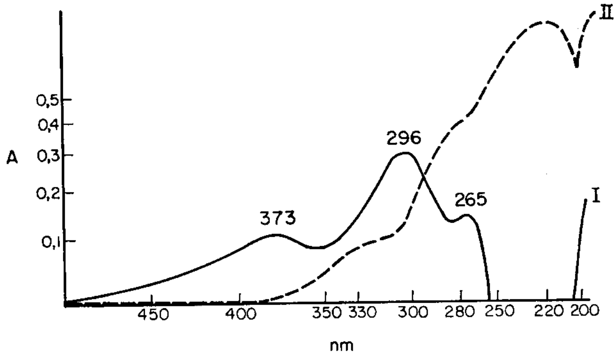

FIG. 2.—Absorbance curves (the substances are dissolved in distilled water);

I. Dimethylaminoethanethiol + palladium chloride, measured against a palladium chloride solution.

II. Palladium chloride solution measured against distilled water.

The method is applicable to aminoalkylthiophosphorus compounds, thio esters and the corresponding thiol compounds, provided that the palladium complexes are soluble in water.

Apparatus

Zeiss spectrophotometer PMQ II

Quartz cells, 1 *cm*

Wavelength, 250 or 315 nm; in most cases 250 nm is preferable.

Reagents

Palladium chloride solution. $0{\cdot}05M$ (ammonium chloropalladite, Specpure, Johnson, Matthey & Co. Ltd., London), in $0{\cdot}3M$ hydrochloric acid.

Hydrochloric acid. $0{\cdot}3M$

Standard solution for the calibration curve. The thiol compound to be measured, *e.g.*, dimethylaminoethylthiodiethoxyphosphine oxide dissolved in isopropanol.

Reference solution. 0·5 Ml of the palladium chloride solution diluted to 50 ml with $0{\cdot}3M$ hydrochloric acid.

Calibration curve

Measure 0·5 ml of the palladium chloride solution into each of five 50-ml volumetric flasks. Add known amounts of the standard solution to cover a concentration range between 2×10^{-6} and $2 \times 10^{-4}M$. Make up to the mark with $0{\cdot}3M$ hydrochloric acid. Measure the absorbance at 250 and 310 nm against the reference solution and plot the calibration curve.

Procedure

Dissolve the sample in any solvent that is soluble in water and has zero absorbance in the wavelength range to be used. Measure 0·5 ml of the palladium solution into a 50-ml volumetric flask, add a known amount of the sample solution and make up to the mark with $0{\cdot}3M$ hydrochloric acid. Measure the absorbance at 250 or 310 nm against the reference solution and calculate the result from the calibration curve.

Titrimetric Method

For a direct titration an instantaneous reaction is necessary. Because palladium ions react instantaneously with thiols but not with most other sulphur compounds, thiols may, therefore, be titrated in the presence of organic sulphides; the palladium ion concentration will be too low during the titration to decompose other organic sulphur compounds (*e.g.*, aminoalkylthiophosphine oxides, thiocholine esters, *etc.*). The equivalence point is indicated by the reaction of *p*-nitrosodimethylaniline[7] with excess palladium ions. A bright red complex is formed which is visible at a palladium ion concentration of $10^{-6}M$.

To be titratable the palladium complex of a thiol must have a solubility in 0·3*M* hydrochloric acid of at least 2×10^{-3} mole/litre. The titration should preferably be performed in a recording photometric titrator, but can also be carried out manually. The apparatus used was an EEL titrimeter, modified to enable a recorder to be connected.[8] A typical titration curve is shown in Fig. 3; it is preferable to choose the equivalence point in the middle of the slope of the curve. The standard deviation is $0{\cdot}02 \times 10^{-5}$ mole when a total of $1{\cdot}5 \times 10^{-5}$ mole of thiol are titrated. For titration of aminoethanethiols, for instance, the burette speed was $2{\cdot}966 \times 10^{-3}$ ml/min and the paper speed on the recorder 1·055 cm/min.

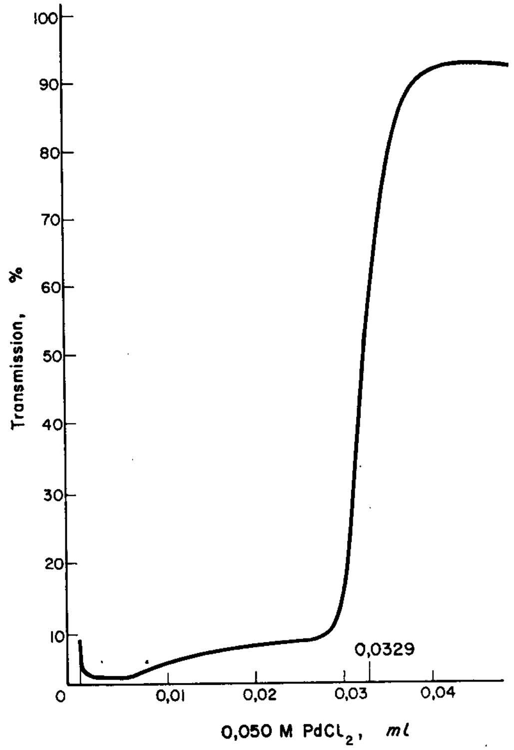

Fig. 3—Titration of 0·50 ml of a $3{\cdot}26 \times 10^{-2}M$ dimethylaminoethanethiol solution with 0·050*M* palladium chloride solution.

Apparatus

EEL titrimeter with filter No. 603 (absorption maximum 490 nm). The apparatus is equipped with an amplifier[9] and is connected to a recorder (Honeywell Brown) and an Agla syringe supplied with a motor-driven gear-box.[9]

Reagents

Palladium chloride solution. 0·0500*M* (ammonium chloropalladite, Specpure) in 0·3*M* hydrochloric acid; standardise the solution against cysteine hydrochloride.

Cysteine hydrochloride. 0·0100*M* (Roche, pro. anal.) dissolved in 0·3*M* hydrochloric acid.

Indicator solution I. Dissolve 0·5 g of *p*-nitrosodimethylaniline in 100 ml of ethanol. The solution should be used within 10 days.

Indicator solution II. Dilute indicator solution I with ethanol 1:10 (stable for 1–2 days).

Procedure

Add to the cylindrical cell of the apparatus 0·15 ml of indicator solution II, 1 ml of 0·3*M* hydrochloric acid and 15 ml of ethanol in that order. To avoid oxidation of the thiol during the titration pass nitrogen through the solution; the bubbles serve at the same time to agitate the solution. Turn on the nitrogen and about 5 min later add 0·01–1·00 ml of the sample solution containing 10^{-5}–3×10^{-5} mole. Set the gear-box of the burette at a suitable speed and the recorder at a suitable paper speed. The complex constants defining the equivalence point have not been determined. We have, however, for empirical reasons, chosen the equivalence point in the middle of the slope. The error will be of minor importance because the slope is very steep. One mole of palladium chloride corresponds to one mole of thiol.

DISCUSSION

By means of the two methods described it is possible to determine organic sulphur compounds that can be decomposed by palladium ions to palladium–thiol complexes. With the photometric method the sum of the original thiol contamination of the organic sulphur compound and the thiol formed during the reaction with the palladium ion can be determined, whereas the titrimetric method gives only the original thiol contamination. For the methods to be applicable, the palladium complexes formed must be soluble in the solvent used. All thiols meeting this requirement and sulphur compounds that can be converted to thiols can be determined by the methods. Parathion and Systox can be determined photometrically if enough time is allowed for complete reaction. Cysteamine, cysteine and certain aminoalkanethiols have been assayed titrimetrically by the method. On the other hand, dodecanethiol has presented difficulties, because of its low solubility.

Disulphides and sulphides present in the sample solution disturb the titrimetric determination only to a negligible extent, provided that their concentrations are low. In some experiments a concentration of 30 mole-% of disulphide which was present gave values which were 2% too high.

Whether the photometric method can be of use for organic sulphur compounds will depend on the velocity of their reaction with the palladium ion. This is easily found by adding the palladium reagent to the sample and measuring the absorbance at regular intervals.

Zusammenfassung—Zwei Analysenvorschriften werden angegeben, die auf der Reaktion von Palladium(II) mit Mercaptanen, Thiocholinestern und Thiophosphorverbindungen beruhen. Die eine Methode ist eine photometrische; gemessen wird die Extinktion des Palladium-Mercaptan-Komplexes, der sich bei Zusatz von Palladiumchlorid zu einer Lösung eines Thiocholinesters oder einer Thiophosphorverbindung bildet. Die zweite Methode, die zur Bestimmung von Thiolen verwendet wird, besteht in einer Titration mit Palladiumchloridlösung als Titriermittel.

Résumé—Deux méthodes sont décrites, basées sur les réactions du ion de palladium(II) aux composés de thiol, aux esters de thiocholine et aux composés de thiophosphore. L'une de ces méthodes est photométrique, et la substance mesurée se compose du complexe de palladium-thiol qui se produit quand on ajoute du chlorure de palladium à une solution d'un ester de thiocholine ou d'un composé de thiophosphore. L'autre méthode, employée pour déterminer les composés de thiol, est titrimétrique, avec une solution de chlorure de palladium comme solution titrante.

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LIQUID–LIQUID, DISCONTINUOUS, COUNTER-CURRENT SOLVENT EXTRACTION FOR DETERMINATION OF TRACE CONSTITUENTS IN GEOLOGICAL MATERIALS—I

EXTRACTION WITH SOLVENTS LIGHTER THAN WATER

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Summary—A new analytical technique for the determination of trace constituents in silicate rocks has been developed. This consists of the use of liquid–liquid, discontinuous, counter-current, solvent extraction in which the chloro-complexes of a number of elements are extracted into a ketonic solvent. Extraction into methyl isobutyl ketone is followed by spectrographic analysis of the contents of the individual extraction tubes, from which a series of extraction curves is plotted. These curves show that trace constituents of a silicate rock can be separated from the main constituents and can be fractionated from eachother. By the use of a solution of a granite-gneiss in 3*M* hydrochloric acid and varying concentrations of this ligand as the aqueous phase in the extraction train, it is shown that a number of trace constituents can be isolated and hence enriched from the rock solution. The method appears to have the advantages of speed, flexibility, relative freedom from contamination and the fact that even weakly-extracted elements may be determined quantitatively. It is suggested that the technique may be suitable not only for the analysis of trace constituents in silicate rocks, but also as a separation method in radioactivation analysis. A further application may be the separation of different oxidation states of the same element, *e.g.*, antimony(III) from antimony(V).

INTRODUCTION

In recent years there has been an increasing interest in the determination of trace elements in geological materials. This is due in the main to the development of more sensitive methods of analysis, *e.g.*, radioactivation, X-ray fluorescence, isotope dilution, *etc.*

Another approach to the problem has been the development of ion-exchange enrichment of the trace constituents, followed by spectrochemical analysis.[1–2] Solvent extraction enrichment methods have also received attention[3–4] and are likely to increase in the future in view of their simplicity and relative freedom from contamination.

Craig and Post[5] have developed a suitable apparatus for discontinuous, counter-current, solvent extraction but the potentialities of this technique for inorganic systems have been largely overlooked. Such systems as have been investigated appear to be largely confined to separation of the rare earths.[6–9]

Werning *et al.*[10] have used the technique for the separation of tantalum from niobium. Recently, Ishimori[11] has used counter-current solvent extraction for the separation of ^{233}U and ^{233}Pu from thoria. To date, there appears to be no literature concerning possible geochemical applications of the technique.

In the work which is now described, a preliminary study has been made of the application of counter-current solvent extraction of the chloro-complexes of certain elements into methyl isobutyl ketone (MIBK). MIBK was chosen for these investigations because of its cheapness, ready availability and known property of being able to extract the chloro-complexes of certain metals.[12]

By analogy with the absorption of chloro-complexes onto an anion-exchange resin,[13] it was to be expected that a number of elements present normally in low concentrations in rocks and minerals would extract into the organic solvent; whereas, of the major constituents, only iron would be likely to extract.

EXPERIMENTAL

Apparatus

Solvent-extraction operations were carried out with a fully-automatic, discontinuous, counter-current extraction apparatus comprising 120 tubes.[5] The individual extraction tubes were mounted on a shaking rack whose axis was attached to an automatic control unit which automatically effected the operations of shaking, settling and decantation. Individual tubes had a capacity of 20 ml for the stationary lower phase and the upper moving phase was fed into the system at the end of each shaking and decantation cycle by means of a 20-ml dispenser attached to a 10-litre reservoir. After each shaking operation, the rack was tilted through 90° and the upper phase decanted into the next extraction tube. The cycle was then repeated. In all cases the contents of individual tubes or sets of tubes were taken to dryness, sodium chloride was added as carrier and the residues were examined spectrographically in the d.c. arc using anode excitation.

Procedures

Initial experiments were carried out with stock solutions containing the following elements: copper, silver, gold, cadmium, gallium, indium, thallium, tin, lead, bismuth, iron, molybdenum, platinum, iridium, palladium (1000 ppm); antimony, vanadium, rhenium, osmium, ruthenium, rhodium (5000 ppm); zinc, arsenic (10,000 ppm); mercury (20,000 ppm). The stock solutions were treated with chlorine gas to ensure that all elements were in their highest oxidation states.

A solution of the elements in 20 ml of $2M$ hydrochloric acid was placed in the first extraction tube and 20 ml of pure hydrochloric acid in each of the following 49 units. The acid solutions were, in all cases, pre-equilibrated with MIBK before use. The solvent, which had also been pre-equilibrated with $2M$ acid, was fed into the system from the reservoir and counter-current extraction was carried out for 50 transfers. The total contents of each tube were then examined spectrographically. The experiment was repeated with $3M$ hydrochloric acid as the aqueous phase. In a further experiment, a solution of the metals in $3M$ hydrochloric acid was placed in the first tube and pure acid of the same strength was added to the next 9 tubes. The subsequent 4 sets of 10 tubes contained $2M$, $1M$ and $0{\cdot}5M$ hydrochloric acid and pure water, respectively.

Although redistilled analytical reagent grade hydrochloric acid was used in the experiments, faint traces of lead, silver and tin were detected in all tubes but were taken into account when plotting distribution curves. A blank run with pure water in place of the hydrochloric acid showed very faint traces of lead in the tubes.

The distribution curves of a number of elements for each experiment were plotted from the spectrographic data and are shown as curves A, B and C in Fig. 1. To avoid confusion in the plot, not all extracted elements are shown.

In a later experiment, 60 ml of a solution of a granite-gneiss (from Charleston, Westland, New Zealand), was prepared in $3M$ hydrochloric acid and placed in the first three extraction tubes. This represented 6% of the total number of tubes and is the maximum permissible for 50 transfers without undue disturbance of the theoretical distribution pattern.[14] The following 7 tubes contained pure $3M$ hydrochloric acid and the arrangement of the aqueous phases in the remaining tubes was exactly as in the previous experiment.

After counter-current extraction with 50 transfers, the tubes were divided into 4 fractions as follows:—

Fraction 1:	Tubes 1–5;
Fraction 2:	Tubes 6–20;
Fraction 3:	Tubes 21–26;
Fraction 4:	Tubes 27–50.

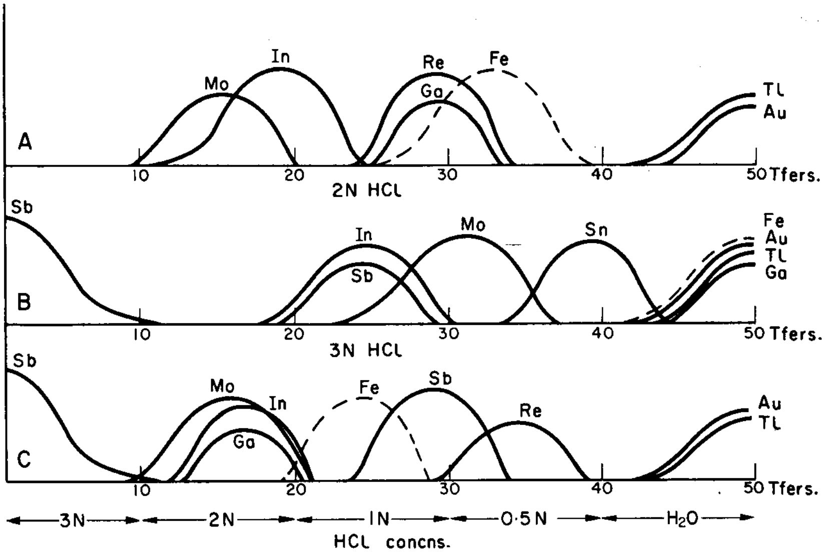

Fig. 1—Distribution curves for a number of elements after counter-current extraction from hydrochloric acid solutions.

The samples were taken to dryness, collected in a matrix of 20 mg of sodium chloride and examined spectrographically. Fraction 1 contained the bulk of the unextracted material. The distribution of the elements is shown in Table I.

TABLE I.—DISTRIBUTION OF ELEMENTS IN EXTRACTS OF A GRANITE–GNEISS SOLUTION AFTER 50 TRANSFERS WITH COUNTER-CURRENT SOLVENT EXTRACTION

Fraction	Tube no.	Cations detected
1	1–5	Ca, Al, Mg, Na, K, Ti
2	6–20	Zn, Ga, In, Mo
3	21–26	Ga, Sn, In, Mo, Fe
4	27–50	Sn, Ni

DISCUSSION

The experiments have clearly demonstrated that separation of trace constituents from the major elements in a rock and from each other is readily feasible with the aid of counter-current solvent extraction.

This form of extraction has a number of advantages over certain other enrichment techniques such as ion-exchange.

(a) The difficulty of completely removing absorbed ions, so commonly encountered in ion exchange, does not arise.

(b) The method is significantly free from contamination dangers because the operations are simple and involve only two reagents, both of which can be readily purified by distillation.

(c) It is now possible to separate quantitatively, ions which are only weakly extracted, provided that the extraction is sufficiently great for them to be removed from the tube or tubes initially containing the sample. This separation can always be achieved by increasing the number of transfers.

(d) The method is extremely flexible in that not only is there a wide choice of ligands and solvents, but also it is a simple matter to alter the nature or concentration of the ligand during the extraction sequence as has been shown above.

A disadvantage of the method lies in the fact that a fully-automatic Craig unit is required for the experimental procedure. However, such units, if obtained, may also be used for separations in organic chemistry for which they were originally designed and hence a certain economy may be achieved.

It would seem that counter-current solvent extraction should have wide applications in geochemical trace analysis. In the experiments with MIBK, the only major element extracted simultaneously with the trace constituents appears to be iron. The presence of this element would normally cause difficulties in the later stages of the analytical procedure. It can be seen from Fig. 1, however, that iron may be separated from other constituents merely by varying the concentration of the ligand. Thus, where iron was originally associated with gold, gallium and thallium (curve B), it now becomes effectively separated from two of these elements (curve C).

Counter-current extraction may also prove to be a useful technique in radioactivation analysis. Even after 50 transfers, it is clear that gold and thallium are effectively separated from all other constituents. This should afford a speedy and reliable method of separating either or both these elements from an irradiated sample without the need for a carrier.

It is interesting to note in Fig. 1, that different oxidation states of the same element may apparently be separated from each other. This can be done where the two separate extraction curves presumably represent antimony(III) and antimony(V).

Because preliminary work on a granite-gneiss has shown the geochemical application of the method, futher investigations are being undertaken with a view to the quantitative determination of a number of trace elements in a suite of silicate rocks.

In a later paper, the geochemical applications of counter-current solvent extraction with solvents heavier than water will be discussed.

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Zusammenfassung—Ein neues analytisches Verfahren zur Bestimmung von Spurenbestandteilen in Silikatgesteinen wurde entwickelt. Es besteht in einer diskontinuierlichen Gegenstrom-flüssig-flüssig-Extraktion, bei der die Chlorokomplexe einiger Elemente in ein Keton extrahiert werden. Nach der Extraktion in Methylisobutylketon wurden die Inhalte der einzelnen Extraktionsgefäße spektrochemisch analysiert; daraus wurde eine Reihe von Extraktionskurven konstruiert. Diese Kurven zeigten, daß Spurenbestandteile in Silikatgesteinen von den Hauptbestandteilen getrennt sowie untereinander fraktioniert werden können. An Hand einer Lösung eines Granit-Gneises in 3n HCl und wechselnden Konzentrationen von Chlorid in der wäßrigen Phase der Extraktionsbatterie wurde gezeigt, daß eine Anzahl von Spurenbestandteilen isoliert und aus der Gesteinslösung angereichert werden können. Die Methode zeigt die Vorteile, daß sie schnell, anpassungsfähig und relativ frei von Möglichkeiten zur Verunreinigung ist, sowie die Tatsache, daß auch nur schwach extrahierbare Elemente quantitativ bestimmt werden können. Es wird die Ansicht vorgetragen, daß das Verfahren nicht nur für die Analyse von Spurenbestandteilen in Silikatgesteinen, sondern auch als Abtrennmethode bei der Radioaktivierungsanalyse geeignet sein könnte. Eine weitere Anwendung kann die Trennung verschiedener Oxydations-stufen des selben Elements sein, wie z.B. Sb^{3+} von Sb^{5+}.

Résumé—On a élaboré une nouvelle technique analytique pour le dosage de constituants à l'état de traces dans les roches aux silicates. Elle consiste en l'emploi d'une extraction par solvant en milieu liquide, discontinue et à contre-courant, au cours de laquelle les chloro complexes d'un certain nombre d'éléments sont extraits dans un solvant cétonique. L'extraction en méthyl-isobutylcétone est suivie d'une analyse spectrochimique du contenu de chaque tube d'extraction, permettant le tracé d'une série de courbes d'extraction. Ces courbes montrent que les constituants à l'état de traces d'une roche aux silicates peuvant être séparés des constituants principaux, et fractionnés. En utilisant une solution de granit-gneiss en HCl 3N, et en variant les concentrations de ce complexe en phase aqueuse dans l'ensemble d'extraction, on a montré qu'on peut isoler un certain nombre de constituants à l'état de traces à partir de la solution de roche, puis procéder à leur enrichissement. La méthode présente les avantages suivants: rapidité, souplesse, elle est relativement exempte de contamination, et même des éléments faiblement extractibles peuvent être déterminés quantitativement. On suggère que la technique peut convenir, non seulement à l'analyse de constituants à l'état de traces dans les roches aux silicates, mais comme méthode de séparation en analyse par radioactivation. On peut en outre l'appliquer à la séparation d'un même élément à divers degrés d'oxydation, par exemple Sb^{3+} et Sb^{5+}.

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LIQUID–LIQUID, DISCONTINUOUS, COUNTER-CURRENT SOLVENT EXTRACTION FOR DETERMINATION OF TRACE CONSTITUENTS IN GEOLOGICAL MATERIALS—II*

EXTRACTION WITH SOLVENTS HEAVIER THAN WATER

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Summary—A new analytical technique has been developed for the determination of trace elements in sea water and other natural waters. The method consists of the use of liquid-liquid, counter-current, solvent extraction with solvents heavier than water. Relatively large volumes of sea water form the moving aqueous layer in the extraction procedure, whereas the lower stationary layer comprises the chelating agents dithizone or 8-hydroxyquinoline dissolved in carbon tetrachloride and chloroform, respectively. Elements are progressively absorbed from the sea water as the aqueous layer passes along the extraction train. Trial experiments with sea water containing additives shows that solutions of 8-hydroxyquinoline and to a lesser extent dithizone are capable of quantitatively retaining a number or elements in a small number of extraction tubes. An experiment has been carried out with a sample of pure sea water from which Mn, Pb, Mo, Sn, Ni, Al, V, Ag, Zn and La were quantitatively extracted into a solution of 8-hydroxyquinoline in chloroform; the elements were all determined spectrographically. It is considered that the method should have wide applications in the analysis of trace elements in sea water because enrichment factors of 400,000 are obtained for the concentrations of these elements. The technique is simple and comparatively free from contamination dangers.

INTRODUCTION

In an earlier paper,[1] the use of liquid–liquid, discontinuous, counter-current solvent extraction enrichment techniques has been proposed as a new technique for trace analysis in geochemistry. This work has hitherto been confined to extraction of solutions of silicate rocks with solvents lighter than water.

Further investigations have been undertaken with a view to extending the scope of the technique to the enrichment and separation of trace constituents from sea water and other natural waters.

The analysis of trace constituents in sea water has been stimulated by the development of new sensitive analytical tools, such as radiochemical and radioactivation analysis,[2–4] atomic absorption or flame photometry[5–6] and isotope dilution. However, despite these new methods, the analysis of many trace elements in sea water has not proceeded much beyond their detection.[7] Lal *et al.*[8] have employed a method involving *in situ* extraction of certain elements onto a hydrated iron(III) oxide gel, but most existing methods depend on some technique of concentration from a

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* Part I: see reference 1.

relatively large volume of sea water coupled with a suitably sensitive analytical procedure.[9–11] For the analysis of trace elements in many natural waters, a high degree of enrichment can be obtained merely by evaporation of the sample to dryness.[12] However, the high salinity of sea water renders this procedure impracticable and clearly, in such cases, there is scope for new and improved methods of extraction.

In the investigations which are now to be described, it has been shown that counter-current solvent extraction can be used for the enrichment of trace constituents from sea water by the use of solvents heavier than water as the lower stationary phase. The basis of the procedure is a reversal of the normal arrangement of counter-current extraction in that the solvent is placed in the extraction tubes and the aqueous sample forms the upper moving layer. In this way, if the aqueous phase were to consist of a large volume of sea water (8 litres) it should be possible for trace constituents to be progressively absorbed from the aqueous phase as it passes through the extraction tubes. The procedure is rendered possible by the fact that none of the major constituents of sea water is extracted strongly into the organic phase.

EXPERIMENTAL

Apparatus

This was as described previously.[1]

Procedures

Initial experiments were carried out with a 0·05% solution of dithizone in carbon tetrachloride. The aqueous phase consisted of 8 litres of sea water at a pH of 7·5 to which had been added small amounts of the following elements: copper, gold, silver, cadmium, gallium, indium, thallium, tin, lead, bismuth, iron, molybdenum, platinum, iridium, palladium (2 mg each); antimony, vanadium, rhenium, rhodium, osmium (10 mg each); zinc, arsenic (20 mg each); mercury (40 mg). To each of 30 extraction tubes was added 20 ml of the organic mixture. In order to avoid loss of carbon tetrachloride because of its very slight solubility in water, the aqueous phase was pre-equilibrated with this solvent. No precautions were necessary for dithizone because it is virtually insoluble in water.

Counter-current solvent extraction was carried out for a total of 400 transfers and the effluent was collected in a suitable container. Visual observation of the dithizone colour showed a conversion from green to red in the first tubes of the extraction train. This coloured front gradually moved along until after 400 transfers it had reached the 20th tube. At the same time, a brown colour developed in the earlier tubes and had replaced the red colour in the first set of three or four tubes by the end of the experiment. The contents of each tube were examined spectrographically after removal of the aqueous layer. The observations indicated quantitative retention of gold, platinum, palladium, copper, thallium and cobalt in the first few tubes of the extraction train. These results are shown in Fig. 1. Cobalt shows displacement along the extraction train and this indicates probable displacement by stronger complexes of other elements.

The experiment was repeated using sea water containing sufficient hydrochloric acid to make the solution 0·1*M* and containing the usual added elements. In this case, because of the lower stabilities of the chelate complexes at low pH,[14] only platinum, gold and palladium were retained quantitatively.

Because dithizone suffers from the disadvantage of being only slightly soluble in carbon tetrachloride so that very little of it can be employed, a search was made for a more suitable chelating agent. The reagent selected for further experiments was 8-hydroxyquinoline (oxine), because this complexes with a large number of ions[15] and is quite soluble in chloroform. An experiment analogous to those carried out previously, was performed with 1% oxine in chloroform as the organic phase and sea water containing the usual additions as the lighter moving phase. Sea water pre-equilibrated with chloroform was treated with 100 ml of saturated chlorine water, because oxine forms complexes only with the higher oxidation states of most elements. This altered the pH to 7·2. Pre-equilibration of the water was effected by the addition of 100 ml of chloroform to the reservoir, which was in constant movement during the extraction. Counter-current extraction was carried out for 400 transfers (8 litres of aqueous phase) with individual shaking times of 2 min, settling times of 0·5 min and decantation times of 0·5 min. Hence, the operation was completed in 20 hr. The tubes were analysed as before and the results, which are shown in Fig. 1, indicated that at least 16 elements had been quantitatively retained in the first 24 tubes. After passage of 8 litres of water, exactly 50% of the oxine had dissolved

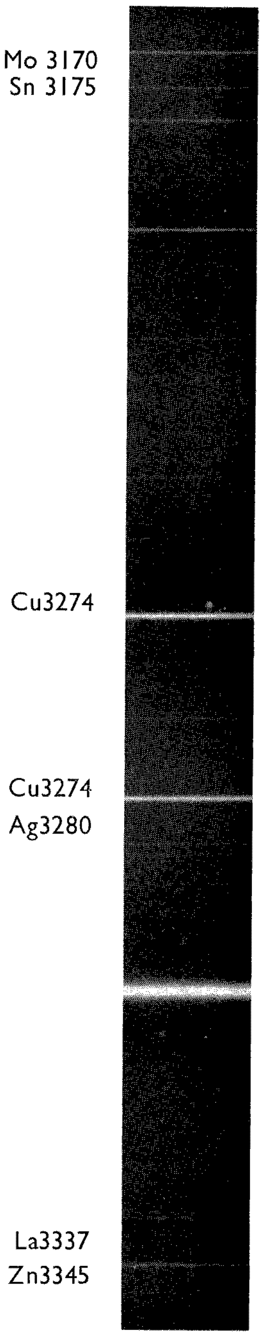

FIG. 2.—Emission spectrum of 8-hydroxyquinoline concentrate from sea water.

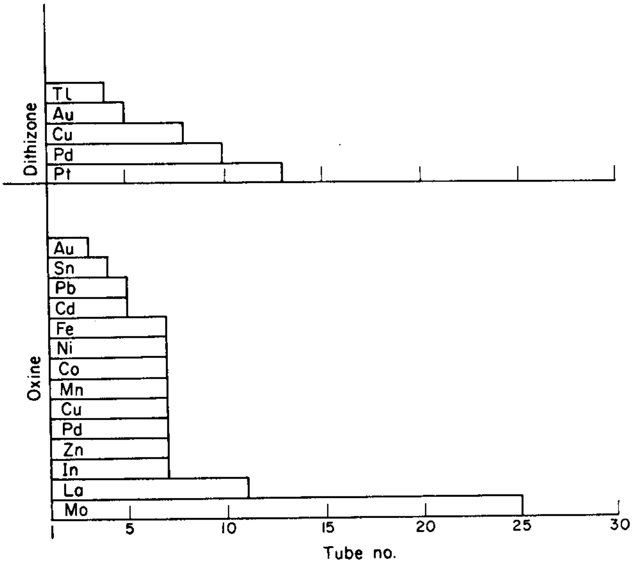

FIG. 1.—Relative retention of elements in extraction tubes containing dithizone or 8-hydroxyquinoline.

out from the organic layer and clearly this will have to be considered in future experiments in relation to the volume of aqueous phase used.

A further experiment was carried out in which pure sea water was used. The conditions were exactly as in the previous trial except that in this instance the organic layers from all the 25 tubes were combined together, taken to dryness and examined spectrographically. The results are shown in Table I.

TABLE I.—ELEMENTS EXTRACTED FROM SEA WATER WITH 8-HYDROXYQUINOLINE IN CHLOROFORM

Element	Pb	Mn	Mo	Sn	Ni	Al	V	Ag	Zn	La
Spectral lines detected, Å	2614 2833	2605 2798	2816 3170	2839 3175	3003 3050	3082 3092	3183 3184	3280 3382	3282 3345	3337 3949

The elements found in the extract were: manganese, lead, molybdenum, tin, nickel, aluminium, vanadium, silver, zinc and lanthanum. Fig. 2 shows an emission spectrum of the sea water extract.

DISCUSSION

The experiments have demonstrated that it is possible to remove selectively trace elements from sea water by use of counter-current solvent extraction with organic phases heavier than water. The total weight of extract from 8 litres of sea water was approximately 20 mg, representing an enrichment factor of 400,000. If this technique were applicable to all trace elements normally found in sea water it should be possible to detect and estimate most of them provided that the extraction technique were coupled with some suitably sensitive analytical system. This is illustrated by consideration of Table II which shows estimated abundances of trace elements in sea water,[7] final concentrations in extract representing an enrichment factor of 400,000 and the spectrographic detection limits of the elements concerned.[16]

If a factor of 10 is allowed to account for variations from expected spectral sensitivities and to allow for sufficient intensities for quantitative determinations, it should be possible to analyse the elements marked with an asterisk in the table by a combination of counter-current extraction and emission spectroscopy. Such calculations are based on a volume of 8 litres of sample and, obviously, greater or lesser volumes may be employed either to increase the sensitivity of the method or to take advantage of a more sensitive system of final analysis.

TABLE II.—EXTRACTION OF TRACE ELEMENTS FROM SEA WATER
(Asterisks indicate elements which should be readily determinable by a combination of the enrichment technique with spectrographic analysis)

	Estimated concn. in sea water (ppm) (Goldberg, 1961)	Concn. if enriched by factor of 400,000, *ppm*	Spectrographic detection limit (ppm) (Ahrens & Taylor, 1960)
Al*	0·01	4000	2
Sc	0·00004	1·6	2
Ti*	0·001	400	10
V*	0·002	800	5
Cr	0·00005	2	1
Mn*	0·002	800	10
Fe*	0·01	4000	5
Co	0·0005	20	10
Ni*	0·002	800	5
Cu*	0·003	1200	0·5
Zn*	0·01	4000	3
Ga	0·00003	1·2	3
Ge	0·00007	28	5
As*	0·003	1200	100
Rb*	0·12	4800	1
Sr*	8	800,000	5
Y	0·0003	12	10
Nb	0·00001	0·4	30
Mo*	0·01	4000	5
Ag*	0·0003	12	0·5
Cd	0·0001	4	10
In	0·02	8000	1
Sn*	0·003	120	10
Sb	0·0005	20	20
Cs*	0·0005	20	2
Ba*	0·03	12,000	5
La	0·0003	12	10
Ce	0·0004	16	500
W	0·0001	4	20
Au	0·000004	0·2	10
Hg	0·00003	1·2	100
Tl	0·00001	0·4	1
Pb	0·0001	4	5
Bi	0·0002	8	20
Th	0·0037	28	100
U	0·003	120	100

Some of the advantages of counter-current extraction enrichment techniques are enumerated below.

(a) Very high enrichments of the order of 400,000 can be obtained from a volume of approximately 8 litres of sea water.

(b) There is little risk of serious contamination because only two reagents are used, both of which can be easily purified.

(c) The versatility of the method is apparently high. For example, it should be possible to incorporate several chelating agents in the extraction train, either together or in separate tubes in order to increase the number of elements extracted. Greater selectivity can be obtained by varying the pH (as in the case of the dithizone experiments) or alteration of the nature of the chelating agent.

Against these advantages must be set the fact that a fully-automatic counter-current extraction apparatus is necessary for the technique. Such units are relatively expensive but have many other uses, such as in organic separations for which they were originally designed. They can also be used for separation and enrichment of trace elements in silicate rocks using solvents lighter than water.[1]

Although an operating time of 20 hr is comparatively long for one determination, this makes little imposition on the operator's time because the apparatus is fully automatic.

In spite of the fact that only two reagents are used, the sensitivity of the method is likely to be limited by the reagent and container blanks. Blanks carried out on the purified reagents* showed only slight traces of lead among those elements under study. In cases where impurities often extracted from laboratory glassware (*e.g.*, iron, lead, *etc.*) are themselves present in very low concentrations in sea water, the sensitivity of the method will be lowered. In most cases, however, very high enrichments should be capable of achievement. The magnitude of the blank for a particular element could be determined by re-extraction of a once-extracted sample of sea water.

Work is at present being carried out on the application of the method to the quantitative determination of a number of trace elements in specimens of sea water from the oceans around New Zealand.

Acknowledgements—The author is indebted to the New Zealand University Research Committee and the Nuffield Foundation for grants towards the establishment of a spectrographic laboratory at Massey University. He is also indebted to Chemistry Division D.S.I.R., New Zealand for the loan of a 120-tube fully-automatic counter-current extraction apparatus.

Zusammenfassung—Ein neues analytisches Verfahren zur Bestimmung von Spurenelementen in Meerwasser und anderen natürlichen Wässern wurde entwickelt. Es besteht in einer diskontinuierlichen Gegenstrom-flüssig-flüssig-Extraktion mit schwereren Lösungsmitteln als Wasser. Relativ große Meerwasser-Volumina bildeten die bewegte wäßrige Schicht beim Extraktionsvorgang; die stationäre Unterphase bildeten die Chelatbildner Dithizon oder Oxin in Tetrachlorkohlenstoff bzw. Chloroform. Im Verlauf der Wanderung der wäßrigen Phase durch die Extraktionsbatterie wurden einige Elemente immer mehr aus dem Wasser extrahiert. Tests mit Zusätze enthaltendem Meerwasser zeigten, daß Lösungen von Oxin und, in geringerem Ausmaß, von Dithizon eine Anzahl von Elementen in wenigen Extraktionsstufen quantitativ zurückhalten können. Ein Versuch wurde ausgeführt mit einer Probe von reinem Meerwasser; aus diesem wurden Mn, Pb, Mo, Sn, Ni, Al, V, Ag, Zn und La quantitativ in eine Lösung von 8-Hydroxychinolin in Chloroform extrahiert. Alle Elemente wurden spektrochemisch bestimmt. Es wird erörtert, daß die Methode bei der Analyse von Spurenelementen in Meerwasser zahlreiche Anwendungsmöglichkeiten haben wird, da Anreicherungsfaktoren bis 400,000 für diese Elemente gefunden wurden. Das Verfahren ist einfach und relativ frei von Gefahren der Verunreinigung.

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* All chemicals except oxine were purified by distillation. Oxine was purified by vacuum distillation.

Résumé—On a élaboré une nouvelle technique analytique pour le dosage d'éléments à l'état de traces dans l'eau de mer et autres eaux naturelles. La méthode consiste en l'emploi d'une extraction par solvant en milieu liquide, à contre-courant, avec des solvants plus denses que l'eau. Des volumes relativement importantes d'eau de mer forment, dans le procédé d'extraction, la couche aqueuse mobile, cependant que la couche stationaire inférieure est constituée par les agents chélatants dithizone ou oxine, en solution respectivement dans le tétrachlorure de carbone et le chloroforme. Les éléments sont progressivement absorbés de l'eau de mer, tandis que la couche aqueuse traverse l'ensemble d'extraction. Des essais de sondage avec l'eau de mer contenant des additifs ont montré que les solutions d'oxine et, à un degré moindre, de dithizone, sont capables de retenir quantitativement un certain nombre d'éléments dans un petit nombre de tubes d'extraction. Une expérience a été menée avec un échantillon d'eau de mer pure, de laquelle on a extrait quantitativement Mn, Pb, Mo, Sn, Ni, Al, V, Ag, Zn et La dans une solution de 8-hydroxyquinoléine en chloroforme. Les éléments ont tous été dosés spectrochimiquement. On considère que la méthode devrait avoir de larges applications dans l'analyse d'éléments à l'état de traces dans l'eau de mer, des facteurs d'enrichissement de 400,000 ayant été obtenus pour les concentrations de ces éléments. La technique est simple et comparativement exempte de dangers de contamination.

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SPECTROFLUORIMETRIC DETERMINATION OF MICROGRAM AMOUNTS OF THALLIUM

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Summary—Thallium(I) in a concentrated hydrochloric acid-potassium chloride medium shows a violet fluorescence with an excitation maximum at 250 mμ and a fluorescence emission maximum at 430 mμ. This has been applied for the spectrofluorimetric determination of thallium down to the range 0·01 to 0·08 ppm. The interference of 53 ions has been examined at the 100-fold molar excess level. Hydrogen peroxide oxidation to thallium(III) and extraction from 1·5*M* hydrochloric acid into diethyl ether, followed by sulphur dioxide reduction, separates microgram amounts of thallium quantitatively from all interfering cations investigated except antimony(V), bismuth, gold and platinum(IV). Large amounts ($\times 10^6$) of sulphate do not interfere.

SEVERAL colorimetric methods are available for the determination of small amounts of thallium in solution; these utilise the reagents Methyl Violet,[1] Rhodamine B,[2] iodine,[3] dithizone,[4] thionalide[5] and 8-hydroxyquinoline.[6] Onishi[7] has proposed a fluorimetric method for the determination of 2-20 μg of thallium in which the fluorescence of Rhodamine B chlorothallate in benzene solution is measured at 560 mμ. In this method the thallium(III) is extracted into chloroform as thallium dithizonate and then into benzene as Rhodamine B chlorothallate.

The present paper describes the determination of microgram amounts of thallium using the violet fluorescence of the thallium(I) ion in the presence of excess chloride ion in concentrated hydrochloric acid. This fluorescence was first reported by Pringsheim and Vogels[8] and subsequently applied to the detection of thallium in ores and other minerals by Sill and Peterson.[9]* The violet fluorescence was attributed to the existence of the complex anionic $TlCl_3{}^{2-}$ species, with neither H_2TlCl_3 (formed in the presence of considerable acid) nor thallium ion showing any fluorescence. The fluorescence can only be obtained in a medium containing a vast excess of both alkali chloride and hydrochloric acid. It is, therefore, not possible to employ the mole-ratio, slope-ratio and continuous variations procedures to elucidate the nature of the fluorescent species. The fluorescence emission is measured at 430 mμ with an excitation wavelength of 250 mμ in a concentrated hydrochloric acid-potassium chloride medium. Optimum conditions have been established for the determination and the effect of numerous ions has been investigated. An extraction system has been devised which readily separates thallium from the more important interfering ions. Cupferron, 8-hydroxyquinoline and acetylacetone extraction procedures were examined before it was decided that the most efficient and selective separation could be obtained by oxidation of thallium(I) to thallium(III) with hydrogen peroxide

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* After preparation of this manuscript we noted a recent paper by R. Bock and E. Zimmer (*Z. analyt. Chem.*, 1963, **198**, 170) describing the spectrofluorimetry of thallium(I) in strong sodium chloride solution in the absence of hydrochloric acid. Their note contains no interference data and does not describe an analytical procedure.

followed by extraction into diethyl ether from the optimum concentration of hydrochloric acid; thallium(I) cannot be extracted quantitatively from hydrochloric acid into diethyl ether. In the other extraction procedures examined it is difficult to remove the thallium from its cupferron, oxine or acetylacetone complex before the determination. Extraction from 1·5*M* hydrochloric acid separates thallium(III) almost quantitatively from all foreign ions investigated except gold, bismuth, platinum(IV) and antimony(V), which co-extract to varying extents. The efficiency of the separation is further improved by washing the ether extract with an aliquot of 1·5*M* hydrochloric acid which back-extracts traces of, for example, iron(III), which extract with the thallium(III) to an extent of <1 %. The ether phase is then evaporated to dryness and the thallium(III) reduced to the univalent state by gaseous sulphur dioxide before the determination. Although the extraction of thallium(III) chloride into diethyl ether has been applied on a macro scale,[10] the present investigation shows that it can be used successfully for microgram amounts of thallium, with an extraction efficiency of *ca.* 98 % in the range of 1 to 8 μg of thallium.

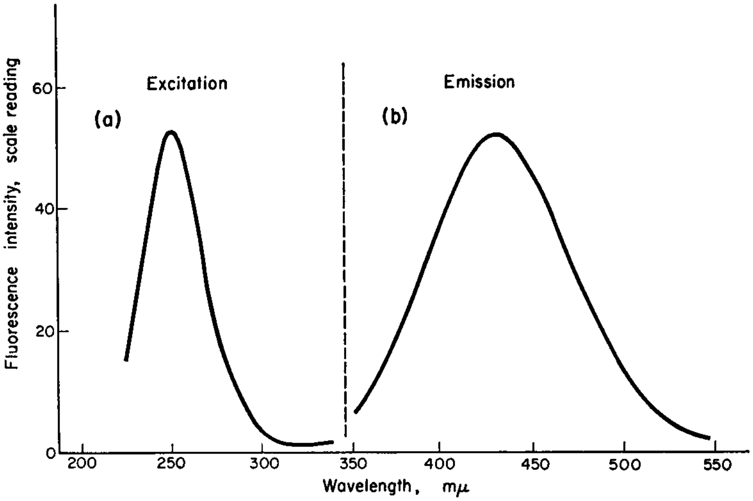

FIG. 1.—Excitation and emission spectra (uncorrected) of thallium(I) complex in HCl-KCl solution [Tl(I) concentration: 2·5 × $10^{-4}M$; sensitivity scale: × 10]:
(A) Emission measured at 430 mμ.
(B) Exciting wavelength set at 250 mμ.

Spectral characteristics

Fig. 1 shows the excitation and emission spectra for the thallium(I) ion in hydrochloric acid-potassium chloride solution. These spectra are uncorrected for variations in the emission characteristics of the lamp and the response characteristics of the photomultiplier. The relevant correction curves are given in Fig. 2. Correction methods are dealt with fully elsewhere by Parker and Rees[11] and their paper may be consulted for guidance. The excitation maximum occurs at 250 mμ and the fluorescent emission maximum at 430 mμ. Fig. 3. shows the emission spectra of more dilute

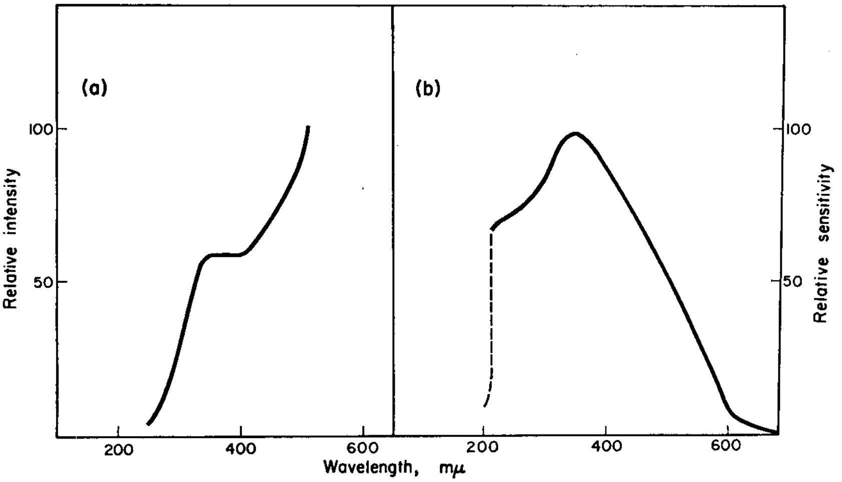

FIG. 2.—Correction curves for variations of lamp intensity and photomultiplier sensitivity with wavelength:

(A) Spectral characteristics of lamp + excitation monochromator (relative intensity against wavelength).

(B) Photomultipler characteristics (relative sensitivity against wavelength).

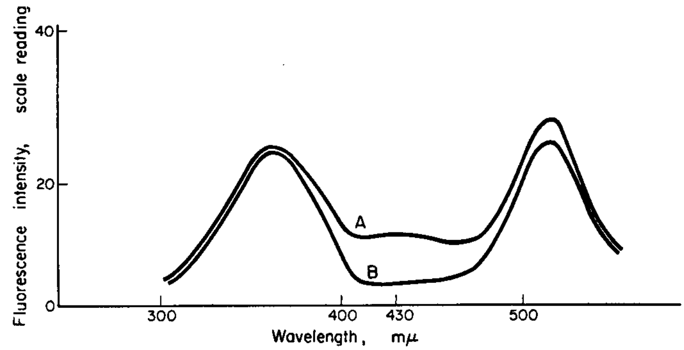

FIG. 3.—Emission spectra (uncorrected) in HCl-KCl solution (exciting wavelength set at 250 mμ; sensitivity scale: × 0·1):

(A) Tl(I) concentration $4 \times 10^{-7}M$.

(B) No Tl(I) present.

solutions (uncorrected) at much increased sensitivity with wide (20 mμ) slits and no protective filters. The peaks at approximately 510 mμ and 360 mμ are attributed to second order diffraction from the analysing (grating) monochromator and stray radiation within the monochromators. The *tails* of these peaks make up the blank *fluorescence* at 430 mμ. The signal at this wavelength is then directly proportional to the thallium concentration. Calibration curves prepared at this level of concentration pass above the origin for the reasons discussed.

Effect of hydrochloric acid and potassium chloride concentrations

The optimum amounts of hydrochloric acid and potassium chloride for the determination were established by varying their concentrations dependently. In a solution $3{\cdot}3M$ in hydrochloric acid, the fluorescence intensity increases with increase of potassium chloride concentration up to 0·8*M*. Above this level, the fluorescence intensity remains constant and potassium chloride tends to precipitate by the common ion effect. It was also shown that in 0·8*M* potassium chloride, a 3·3*M* hydrochloric acid concentration is required to produce maximum fluorescence. Thus, the best solution should be approximately 3·3*M* in hydrochloric acid and 0·8*M* in potassium chloride, *i.e.*, 100 ml of solution contains 30 ml of concentrated hydrochloric acid and 20 ml of saturated potassium chloride.

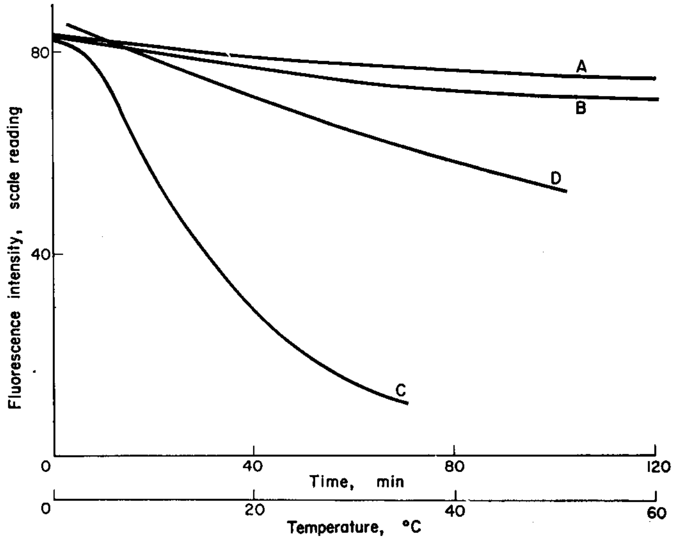

FIG. 4.—Effect of time and temperature on fluorescence intensity:

(A) Variation of fluorescence with time: standing in darkness.
(B) Variation of fluorescence with time: standing in normal laboratory conditions.
(C) Variation of fluorescence with time: continuous irradiation at 250 mμ.
(D) Variation of fluorescence with temperature.

A slight reduction in the fluorescence intensity (<10%) was observed when ammonium chloride or sodium chloride was substituted for potassium chloride in the recommended procedure.

Effect of time

Thallium(I) in a strongly acid medium is oxidised by air to thallium(III) and this process is accelerated by ultraviolet radiation. An $8 \times 10^{-7}M$ solution of thallium(I) prepared by the recommended procedure showed an average reduction in fluorescence intensity of 10% after standing for 2 hr in darkness, and a reduction of 14% after standing for 2 hr under normal laboratory conditions, *i.e.*, under fluorescent tube lighting, while continuous irradiation of the solution at 250 mμ in the spectrofluorimeter completely destroyed fluorescence within 1 hr (*cf.* Fig. 4).

Effect of temperature

Between the limits of the temperature range investigated, *i.e.*, 3–43°, a decrease of fluorescence intensity with increase in temperature of development was found which corresponds to a temperature coefficient of approximately 1 %/°C (*cf.* Fig. 4). Under normal laboratory conditions, all measurements of the thallium fluorescence were made at 23 ±3°, and the observed fluorescence intensities were compared with standards prepared simultaneously, so that the existence of this temperature coefficient did not alter the validity of the results obtained. However, care should be taken to minimise generation of heat of mixing between concentrated hydrochloric acid and water during the preparation of samples for measurement, by adding the acid to as large a volume of water as possible and thoroughly mixing immediately.

Precision

The precision of the method at its maximum sensitivity is compounded of (a) the chemical precision, and (b) the instrumental precision. These were, therefore estimated separately by multiple determinations, (a) using sufficient thallium (80 μg) to give readings on a less sensitive scale (× 0·1) where instrumental *noise* is negligible; and (b) using 8 μg of thallium and measuring directly on the most sensitive scale (× 0·01) where instrumental *noise* is appreciable, without treating the solution by the extraction procedure.

These experiments indicated a chemical precision of ±1·3% and an instrumental precision of ±1·6%.

Accuracy

The data in Table I were obtained from the results of the analysis of solutions for thallium by the recommended procedure (see *Experimental*).

TABLE I.—ANALYSIS OF THALLIUM(I) SOLUTIONS TREATED AS UNKNOWN SAMPLES

	Thallium, μg		Error		
Sample	Present	Found	μg	%	Foreign ions present, μg
1	4·90	4·57	−0·33	−6·6	Fe(III) (5600)
2	6·92	6·72	−0·20	−2·9	Fe(III) (5600)
3	3·87	3·75	−0·12	−3·1	Fe(III) (5600)
4	3·26	3·26	—	—	Fe(III) (5600)
5	5·91	6·13	+0·22	+3·7	Cu(II) (630), Hg(II) (2000)
6	3·67	3·77	+0·10	+2·8	Cu(II) (630), Hg(II) (2000)
7	3·87	4·04	+0·17	+4·4	Cu(II) (630), Hg(II) (2000)
8	4·08	3·89	−0·19	−4·7	Al (2700), Zn (6500)
9	7·14	6·72	−0·42	−5·9	Al (2700), Zn (6500)
10	5·91	5·87	−0·04	−0·6	Be (900), Mg (2400)
11	7·95	7·78	−0·17	−2·1	Be (900), Mg (2400)
12	3·87	3·75	−0·12	−3·1	Al (2700), Ba (13700)
13	6·31	6·11	−0·20	−3·2	Al (2700), Ba (13700)
14	2·24	2·24	—	—	Be (900), Mg (2400)
15	4·28	4·50	+0·22	+5·2	Be (900), Mg (2400)
16	5·10	4·87	−0·23	−4·5	Co (5900), Fe(III) (5600)
17	7·14	6·68	−0·46	−6·5	Co (5900), Fe(III) (5600)

Effect of foreign ions

The effect of 53 foreign ions on the thallium fluorescence in pure solution was studied. None of the cations investigated produced a fluorescence similar to that of thallium, but several, when present in relatively large concentrations, showed fluorescence at different wavelengths, *e.g.*, lead (excitation maximum 290 mμ/fluorescence maximum 480 mμ), copper(I) (390/460 mμ), tin(II) (270/480 mμ) and cerium(III) (250/350 mμ). The effect of a 100-fold molar excess of each ion on the determination of 8 μg of thallium was investigated. After consideration of the reproducibility of the determination of 8 μg of thallium in pure solution, ions were considered to interfere at this level when they caused a variation of fluorescence intensity of $\geqslant \pm 5\%$. The investigation revealed that the following ions do not interfere under the above conditions: aluminium, ammonium, arsenic(III), arsenic(V), barium, beryllium, calcium, cadmium, cobalt, chromium(III), gallium, indium, lead, lithium, magnesium, manganese(II), nickel, scandium, selenium(IV), silver, sodium strontium, thorium, tin(II), titanium(IV), tungsten(VI), vanadium(IV), zinc, zirconium, bromide, fluoride, thiocyanate, nitrate, sulphate and tartrate. A 100-fold excess of the following ions caused the error in the fluorescence intensity given in parenthesis: antimony(V) (−49%), bismuth (−69%), cerium(III) (+900%), cerium(IV) (+900%), copper(II) (−21%), gold (−100%), iron(II) (−25%), iron(III) (−92%), mercury(II) (−28%), molybdenum(VI) (−100%), platinum(IV) (−92%), tellurium(IV) (−32%), tin(IV) (−59%), uranium(VI) (−18%), vanadium(V) (−20%), iodide (+13%), bromate (−100%) and iodate (−100%).

The interfering cations listed above were then taken, normally in large excesses over 8 μg of thallium, through the recommended extraction procedure. The results are shown in Table II.

TABLE II

Cation	Molar excess	Variation in fluorescence intensity[a]
Au	10	−68%
Bi	500	−20%
Pt(IV)	200	−14%
Sb(V)	2500	−100%
Ce(III)	500	$\leqslant \pm 5\%$
Ce(IV)	500	$\leqslant \pm 5\%$
Cu(II)	2500	$\leqslant \pm 5\%$
Fe(II)	2500	$\leqslant \pm 5\%$
Fe(III)	2500	$\leqslant \pm 5\%$
Hg(II)	250	$\leqslant \pm 5\%$
Sn(IV)	250	$\leqslant \pm 5\%$
Te(IV)	2500	$\leqslant \pm 5\%$
U(VI)	500	$\leqslant \pm 5\%$
V(V)	2500	$\leqslant \pm 5\%$

[a] With respect to thallium(I) standard.

Because this method is likely to find application in the determination of thallium in biological and other materials which require dissolution or destruction before determination, the effect of the presence of a large excess (*ca.* 10^6-fold) of sulphate and nitrate on the extraction and determination was investigated. The presence of sulphate ions has no effect on the method, but nitrate ions interfere at this level by co-extraction into diethyl ether with the thallium(III). Large excesses of nitrate (>100-fold molar excess over thallium) must, therefore, be removed by fuming the solution with hydrochloric acid before the determination.

EXPERIMENTAL

Reagents

$10^{-3}M$ *Thallium(I) solution.* Dissolve 0·2525 g of analytical reagent grade Tl_2SO_4 (Hopkin and Williams, Chadwell Heath, Essex, England) in water and dilute to 1 litre, using water from an all-glass distillation apparatus. This stock solution was diluted to $10^{-5}M$ as required.

Hydrochloric acid. Analytical-reagent grade (Hopkin and Williams) was used. Prepare a 2*M* solution by diluting 45 ml of the concentrated acid to 250 ml with water.

Saturated potassium chloride solution. Dissolve *ca.* 150 g of reagent grade potassium chloride (Hopkin and Williams) in 500 ml of boiling water, filter the solution while warm and allow to crystallise on cooling. The saturated solution is approximately 4·1*M* in potassium chloride and was standardised by Volhard's method.

Hydrogen peroxide. Prepare 6% (20 -vol.) solution from general purpose reagent (Hopkin and Williams).

Diethyl ether. Solvent grade (Hopkin and Williams)

Sulphur dioxide. Liquified (Hopkin and Williams)

Foreign ions. 0·1*M*, 0·02*M* or 0·01*M* Solutions of analytical-reagent grade salts were used.

Apparatus

Fluorescence measurements were made with a Farrand spectrofluorimeter (Farrand Optical Co. Cat. No. 104244) in which grating monochromators are used to isolate both the exciting and fluorescent radiation, and fitted with a 150-W xenon arc lamp (Hanovia Div. Cat. No. 901 C-1), an RCA IP 28 photomultiplier and a Honeywell-Brown recorder. Fused quartz cells (10 × 20 × 50 mm) were used throughout the work. Fluorescence was measured at right angles to the incident light such that the mean solution path-length of the exciting radiation is 5 mm and that of the fluorescent emission is 10 mm. 20-Mμ bandwidth slits were used in both the exciting and analysing monochromators, and no filters were used during these experiments.

Determination of thallium

Calibration curve. To 20 ml of saturated potassium chloride solution, 30 ml of water and 30 ml of concentrated hydrochloric acid in a 100-ml volumetric flask, transfer accurately between 0·5 and 4·0 ml of standard thallium(I) solution ($10^{-5}M \equiv 2·04\ \mu$g/ml) and dilute to volume with water. Allow the solutions to stand for 15 min, then measure the intensity of the fluorescence at 430 mμ and an excitation wavelength of 250 mμ. The plot of fluorescence intensity against thallium concentration (0·01–0·08 ppm) is a straight line and passes slightly above the origin. Linearity extends beyond this upper limit to a final concentration of 2 ppm of thallium, *i.e.*, 200 μg in 100 ml of aqueous solution. Prepare and measure two standards with each group of samples, using 0 and 4 ml of the thallium(I) solution (2·04 μg/ml), respectively.

Extraction procedure

Transfer an aliquot of standard thallium(I) solution (0·5–4·0 ml of $10^{-5}M$ solution) to a separating funnel containing 15 ml of 2*M* hydrochloric acid and 1 ml of 20-volume hydrogen peroxide. Extract once into 25 ml of diethyl ether and discard the aqueous phase. Wash the organic phase with 10 ml of 1·5*M* hydrochloric acid and again discard the aqueous phase. Transfer the ether phase to a 100-ml beaker, rinse the separating funnel with a further 10 ml of ether, combine the ether extracts and evaporate to dryness on a water-bath. Dissolve the residue in 50 ml of water, pass gaseous sulphur dioxide into the solution for 5 sec, then evaporate the solution to a volume of 10 ml, after the addition of 1 ml of concentrated hydrochloric acid to assist the removal of sulphur dioxide (Note). Cool the solution, transfer to a 100-ml standard flask containing 20 ml of saturated potassium chloride solution, add 30 ml of concentrated hydrochloric acid, dilute to volume with distilled water and measure the fluorescence after 15 min at 250/430 mμ.

Note. It is essential to ensure complete removal of sulphur dioxide because it has a strong quenching action on the $TlCl_3^{2-}$ ion fluorescence.

Acknowledgment—We wish to thank the Department of Scientific and Industrial Research for the provision of a grant to one of us (T. S. W.) for the purchase of the spectrofluorimeter used in this work and also for providing a Research Studentship to another (C. W.).

Résumé—Le thallium (I), en milieu acide chlorhydrique concentré—chlorure de potassium, présente une fluorescence violette, avec maximum d'excitation à 250 mμ et maximum d'émission de fluorescence à 430 mμ. On a appliqué ce fait au dosage spectrofluorimétrique du thallium jusqu'à des teneurs de 0,01 à 0,08 p.p.m. On a étudié les interférences de 53 ions à des concentrations molaires 100 fois plus élevées. L'oxydation par l'eau oxygénée en thallium (III), et l'extraction en éther diéthylique, à partir d'une solution 1,5*M* en acide chlorhydrique, suivie de réduction au moyen d'anhydride sulfureux, permettent de séparer quantitativement des quantités de thallium de l'ordre du microgramme de tous les cations interférants étudiés, à l'exception de l'antimoine (V), du bismuth, de l'or et du platine (IV). Des quantités importantes de sulfate (× 10^6) n'interfèrent pas.

Zusammenfassung—Thallium (I) gibt in einem Medium aus konzentrierter Salzsäure und Kaliumchlorid eine violette Fluoreszenz mit einem Anregungsmaximum bei 250 mμ und einem Emissionsmaximum bei 430 mμ. Diese Erscheinung wurde zur spektrofluorimetrischen Bestimmung von Thallium bis herunter zum Konzentrationsbereich 0,01–0,08 p.p.m. ausgenutzt. Die Störung von 53 Ionen wurde bei 100-fachem molarem Überschuß untersucht. Oxydation mit Wasserstoffperoxyd und Extraktion aus 1,5 *M* Salzsäure in Diäthyläther mit nachfolgender Reduktion mit Schwefeldioxyd trennt Mikrogrammengen Thallium quantitativ von allen untersuchten störenden Kationen außer Antimon(V), Wismut, Platin(IV) und Gold. 10^6-facher Überschuß von Sulfat stört nicht.

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DÜNNSCHICHT-CHROMATOGRAPHIE—XV*

TRENNUNG VON TERPEN- UND SESQUITERPENALKOHOLEN AUF SILBERNITRAT-KIESELGEL-SCHICHTEN

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Zusammenfassung—Gemische von C_{10}-, C_{15}- und C_{20}- Alkoholen lassen sich auf normalen Kieselgel-Schichten nicht trennen. Auf paraffin-imprägnierten Schichten wurde eine Trennung in Gruppen mit gleicher Kohlenstoffatomzahl möglich. Mit der Gradient-DC konnte nun festgestellt werden, daß mit zunehmender $AgNO_3$-Imprägnierung einer Kieselgel H-Schicht die Trennung derartiger Gemische gelingt. Der optimale und ökonomische $AgNO_3$-Gehalt der Schicht liegt bei 3%. Als Fließmittel dient ein Gemisch von Methylenchlorid-Chloroform-Äthylacetat-n-Propanol (50 + 50 + 5 + 5 V/V). Der Trenneffekt lässt sich durch eine Mehrfachentwicklung noch verbessern.

AUF normalen Kieselgel- oder Aluminiumoxid-Schichten lassen sich Gemische von Mono-, Sesqui- und Diterpenalkoholen nicht oder nur unzureichend trennen. Einen Fortschritt brachte die in unserem Arbeitskreis von Jork hierzu angewendete "reversed phase"-Technik.[1] Hat man die Alkohole aus einem ätherischen Öl abgetrennt, so gelingt es mit dieser Technik schnell, festzustellen, ob C_{10}-, und/oder C_{15}-Alkohole vorliegen. Auch bei der von uns seit Jahren durchgeführten Kombinationsanalyse GLC-TLC ermöglichen die paraffin-imprägnierten Schichten eindeutige Entscheidungen im Ultramikrobereich. Es erschien jedoch wünschenswert, neben der Gasphasenchromatographie (GLC), die sich für die Trennung von Monoterpenalkohol-Gemischen bestens eignet,[2] eine weitere dünnschicht-chromatographische Methode zu haben, mit der man Gemische von Terpen-, insbesondere aber von Sesquiterpenalkoholen zerlegen kann.

Es ist bekannt, daß man in manchen Fällen durch eine Imprägnierung des Adsorbens mit Verbindungen, die Koordinations-, Chelatkomplexe oder Einschlußverbindungen zu bilden vermögen, substanzspezifischere Trennungen erreichen kann. So wird auf dem Lipid-Gebiet seit einigen Jahren bei der Trennung von Fettsäureestern unterschiedlichen Sättigungsgrades von deren Neigung, mit Silberionen labile Koordinationskomplexe zu bilden, Gebrauch gemacht. Das von Winstein und Lucas[3] zur Verteilungstrennung zwischen zwei nicht mischbaren flüssigen Phasen ausgearbeitete Verfahren wurde dann mit gutem Erfolg von de Vries[4] und Morris[5] auf die Kolonnen- und die Dünnschicht-Chromatographie übertragen. Inzwischen liegen hierüber zahlreiche Arbeiten vor.

Nachdem zunächst festgestellt wurde, daß sich bei Verwendung geeigneter Fließmittel auf Kieselgel-Schichten, die mit 20% Silbernitrat imprägniert waren, Ansätze

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* XIV. Mitteilung: *Chem. Ing. Tech.*, 1964, **36,** 941.

zu einer Trennung von Terpenalkoholen ergaben, wurde der Einfluß verschiedenartiger Sorptionsmittel und Fließmittel, sowie der Imprägnierungsgrad untersucht. Über die Einzelergebnisse dieser Untersuchungen wird später berichtet. Hier soll nur über die daraus resultierenden optimalen Versuchsbedingungen berichtet werden. Eine wertvolle Hilfe beim Studium des Einflusses der Silbernitrat-Konzentration auf den Trenneffekt war uns die Gradient-DC.[6] Es wurden zunächst Gradient-Schichten mit einer Silbernitrat-Konzentration von 0 bis 25 % hergestellt und quer zum Gradient chromatographiert. Nachdem sich zeigte, daß eine Verbesserung der Trennung bei einer Konzentration von über 3 % nicht mehr auftritt, wurden Schichten mit einem $AgNO_3$-Gradient von 0–2,5 % verwendet. Wie die Abb. 1 zeigt, beginnt bereits bei einer Konzentration von 1,5 % $AgNO_3$ die Abtrennung des Nerolidols vom Geraniol. Sie verbessert sich mit der Zunahme der Silbernitrat-Konzentration bis 2 % und bleibt dann nahezu gleich. Auch das kritische Paar Guajol/Borneol zeigt ein ähnliches Verhalten. Bei allen weiteren Versuchen wurde nun auf uniformen Kieselgel H-Schichten, die mit 3 % Silbernitrat imprägniert waren, gearbeitet.

Von zahlreichen getesteten Fließmitteln ergaben Gemische von chlorierten Kohlenwasserstoffen, denen ein oder zwei stärker polare Lösungsmittel in kleinen Mengen zugesetzt waren, den besten Trennerfolg. Allerdings ließ sich ein aus 9 Alkoholen bestehendes Gemisch (s. Abb. 2/I) nicht vollständig trennen; Borneol, Daucol und Cuminalkohol liegen hier praktisch zusammen. Erst durch eine Mehrfachentwicklung mit Fließmitteln unterschiedlicher Polarität konnten auch diese 3 Alkohole gut getrennt werden (Abb. 2/III). Für die erste Entwicklung wurde Methylenchlorid-Chloroform-Äthylacetat- n-Propanol (50 + 50 + 5 + 5 V/V) und für die zweite und dritte Entwicklung Methylenchlorid-Chloroform (40 + 60 V/V) verwendet. Es sei jedoch nicht verschwiegen, daß sich unter den bisherigen Versuchsbedingungen eine Reihe der uns zur Verfügung stehenden Terpen- und Sesquiterpenalkohole nicht trennen lassen, so liegen z.B. Cedrol und Maalialkohol, ferner Guajol, Citronellol, Terpineol und Zimtalkohol auf einer Höhe.

Um nun anhand einer größeren Anzahl von Alkoholen unterschiedlichen Sättigungsgrades zu allgemeineren Aussagen zu kommen, wurden zahlreiche, im Handel erhältliche Terpenalkohole und weitere C_5 — C_{20} — Alkohole in die Versuche mit einbezogen. Zunächst wurden sie mit der vorstehend beschriebenen Methode auf ihre Einheitlichkeit geprüft. Hierbei ergab sich, dass zumeist Gemische vorlagen. Zur Zeit laufen Versuche, diese Produkte auf Silbernitrat-Kieselgel-Kolonnen in präparativem Maßstab zu trennen.

Zusammenfassend lässt sich schon beim augenblicklichen Stand der Untersuchungen feststellen, daß die Anwendung von Silbernitrat-Kieselgel-Schichten ein wertvolles Hilfsmittel zur Auftrennung von verschiedenartigen Alkoholen ist. In unserem Arbeitskreis hat sie bei zahlreichen Problemen ihren praktischen Nutzen gegezeigt, so z.B., um den Hydrierungsverlauf von ungesättigten Alkoholen zu verfolgen. Auf die vorteilhafte Verwendung zur Kontrolle der Identität und Reinheit wurde bereits hingewiesen. Darüberhinaus konnten $AgNO_3$-Kieselgel-Schichten mit Erfolg bei anderen Stoffklassen eingesetzt werden und es gelang u.a., Allyl- von Propenylmethoxybenzolen sauber zu trennen.[7]

Die Versuche werden fortgesetzt. Im Rahmen einer späteren Arbeit sollen dann die Ergebnisse anhand eines größeren Materials diskutiert und weitere Anwendungsmöglichkeiten aufgezeigt werden.

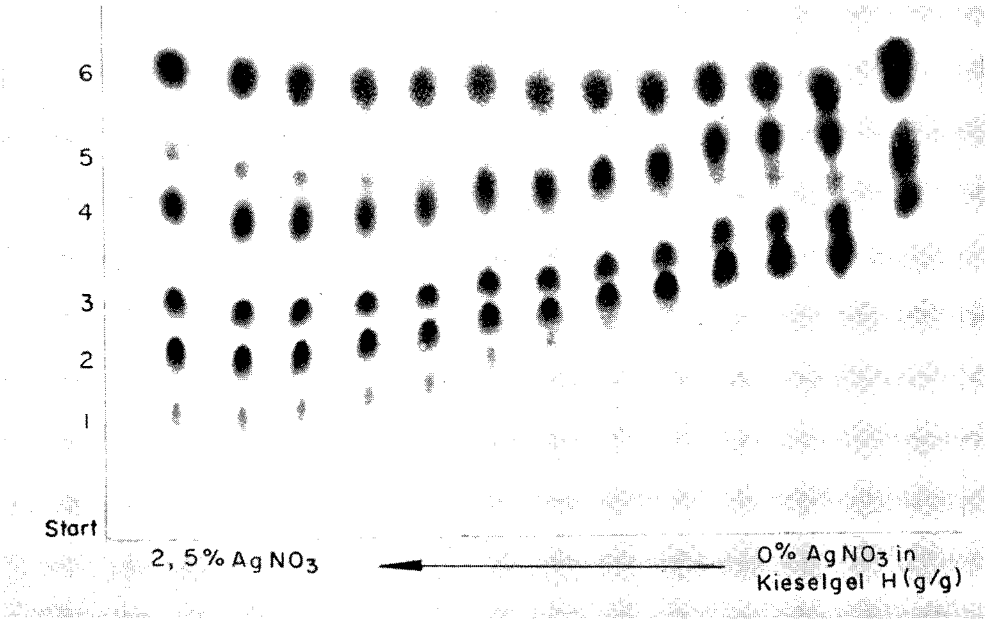

ABB. 1.—Gradient-Schicht-Chromatogramm zur Ermittlung der optimalen $AgNO_3$-Konzentration
(Bezifferung siehe Abb. 2; Einzelheiten im experimentellen Teil).

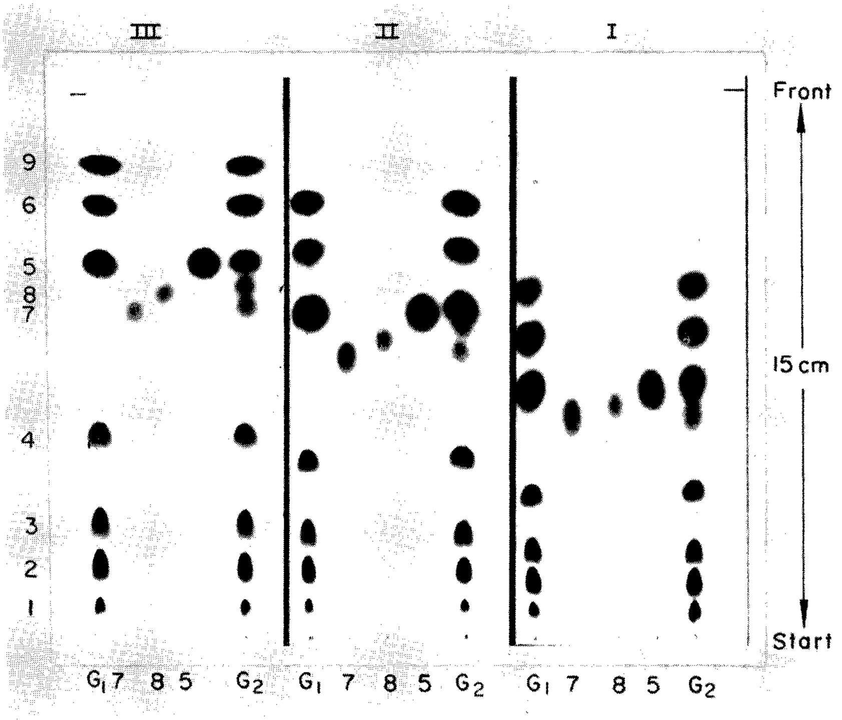

ABB. 2.—Mehrfachentwicklung zur Trennung eines Alkoholgemisches auf einer uniformen AgNO$_3$-Kieselgel-Schicht:

I: Einmalige Entwicklung mit Fließmittel I;
II u. III: Zweite bzw. dritte Entwicklung mit Fließmittel II.

(1 Nerolidol
2 Geraniol
3 Nerol
4 Guajol
5 Borneol
6 Cedrol
7 Cuminalkohol
8 Daucol
9 Carotol
G$_2$ Gemisch 1–9
G$_1$ Gemisch 1–6, 9)

EXPERIMENTELLER TEIL

Herstellung der uniformen Silbernitrat-Kieselgel H-Schichten

Das Beschichten der 20 × 20 cm DC-Platten erfolgte mit der Desaga-Grundausrüstung nach der Standardmethode[8]. 25 g Kieselgel H nach Stahl für die Dünnschicht-Chromatographie der Fa. Merck wurden mit 65 ml Wasser, in dem zuvor 750 mg $AgNO_3$ p.a. "Merck" gelöst waren (= 3% g/g) homogen angerührt. Zum Ausstreichen wurde ein aus V4A-Stahl hergestelltes Streichgerät benutzt.

Herstellung der Gradient-Schichten

Durch Einbau der Mischwelle und Aufsetzen des Teilers wurde das normale Streichgerät in den GM-Streicher verwandelt. In einem Kolben wurden 18 g Kieselgel HF_{254} mit 45 ml Wasser gemischt. In einem zweiten Kolben wurden 18 g Kieselgel H (ohne Fluoreszenzindikator!!) mit 45 ml Wasser, in dem die gewünschte Silbernitratmenge (2,5 bzw. 25% g/g) gelöst ist, gemischt. Darauf wurden die beiden Suspensionen jede in eine der beiden Teilerkammern des GM-Streichers gleich hoch eingefüllt. Nach Herausnehmen der Trennwand wurde die Hülse mittels Kipphebel in Füllstellung gebracht. Das Mischen erfolgte mit einem Antriebsmotor jeweils 30 Sekunden mit und gegen den Uhrzeigersinn. Das Ausstreichen wurde auf einer genau waagerechten Arbeitsschablone vorgenommen.

Prüfung des Gradient-Verlaufs

Die Gradient-Schichten wurden im kurzwelligen UV-Licht betrachtet und es war an der gleichmäßigen Abnahme der Fluoreszenzintensität ein kontinuierlicher Übergang erkennbar.

Trocknung und Chromatographie

Die beschichteten Platten wurden bei 110°C getrocknet, (30 min). Die Aufbewahrung erfolgte unter Lichtabschluß im Exsikkator über Blaugel. Zur Chromatographie wurde die normale Desaga-Trogkammer mit Filtrierpapierauskleidung (Kammersättigung) verwendet. Die Laufstrecke betrug in allen Fällen, auch bei der Mehrfachentwicklung, 15 cm.

Fliessmittel: Zur Herstellung der Fließmittelgemische wurden Lösungsmittel der Firma Merck "zur Chromatographie" oder "zur Analyse" verwandt.

Fließmittel I: Methylenchlorid-Chloroform-Äthylacetat-n-Propanol (50 + 50 + 5 + 5 V/V).

Fließmittel II: Methylenchlorid-Chloroform (40 + 60 V/V). Aufgetragene Mengen: Die Alkohole wurden 1% g/V in Toluol gelöst. Zumeist wurden 0,3 – 1,0 μl (= 3–10 μg) mit der 10 μl Spezialpipette aufgetragen.

Sichtbarmachung: Phosphormolybdänsäure p.a. "Merck" wurde 20% in Methanol gelöst und 10 ml je Platte (20 × 20) cm aufgesprüht. Die besprühten Chromatogramme wurden 5–10 min auf 110°C erwärmt; die Alkohole treten als blaue Flecken auf gelbem Grund hervor.

Summary—Mixtures of C_{10}-, C_{15}- and C_{20}- alcohols cannot be separated on normal silica-gel layers. A separation into groups with the same number of carbon atoms is possible on paraffin-impregnated layers. With gradient thin-layer chromatography it has been established that with increasing silver nitrate impregnation of silica gel, the separation of such mixtures is possible. The optimum and economic silver nitrate content is 3%. As solvent is used a mixture of methylene chloride-chloroform-ethyl acetate-n-propanol (50 + 50 + 5 + 5 v/v). The separation may be improved by multiple development.

Résumé—Des mélanges d'alcools en C_{10}, C_{15} et C_{15} et C_{20} ne peuvenpas être séparés sur des couches de gel de silice normales. Une séparation en groupes à même nombre d'atomes de carbone est possible sur couches imprégnées de paraffine. Par chromatographie sur couche mince à gradient, on a établi qu'avec une imprégnation croissante en nitrate d'argent du gel de silice, la séparation de tels mélanges est possible. La teneur en nitrate d'argent optimale et économique est de 3%. On utilise, comme mélange de solvants, un mélange chlorure de méthylène–chloroforme–acétate d'éthyle–n-propanol (50 + 50 + 5 + 5 v/v). On peut améliorer la séparation par développement multiple.

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TALANTA REVIEW*

APPLICATIONS OF NUCLEAR AND ELECTRON MAGNETIC RESONANCE IN ANALYTICAL CHEMISTRY

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Summary—The principles of nuclear and electron magnetic resonance are briefly described, with reference to the use of these techniques in analytical chemistry. A wide field of analytical applications is reviewed in order that the scope and limitations of the methods may become apparent.

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I. INTRODUCTION

THE widespread interest in nuclear and electron magnetic resonance techniques, which has been such a striking feature of chemical progress in the last decade, has centred

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* For reprints of this review see Publisher's Announcement at the end of this issue.

largely on the important contributions made by these techniques to the solution of structural problems in organic chemistry and, in the case of electron resonance, to the very detailed information which it has provided on the electronic structure of free radical species. The applications of both techniques to problems in analytical chemistry has been much less rapid, although the characteristic nature of the spectra observed left no doubt, from the outset, of the potential importance of both techniques, at least in qualitative analysis. The reason for this comparatively slow growth in analytical applications lies mainly in the stringent requirements in instrumental stability and sensitivity when information of a quantitative nature is required. In the past few years these requirements have been adequately met by commercially available spectrometers, and the way is open for rapid advance.

The present review is designed to cover a wide field of analytical applications in order that the scope and limitations of the methods may become apparent. Only sufficient of the theory is included to permit some understanding of the requirements of the techniques when quantitative information is sought, and to provide, at the same time, a brief introduction to the terminology involved.

II. NUCLEAR MAGNETIC RESONANCE

(*A*) *Principles*

When a sample with nuclei possessing magnetic moments is placed in a strong uniform magnetic field, such that it experiences a field H_0, and is irradiated with energy in the radiofrequency (rf) range, transitions are induced between the possible orientations of the nuclear spins in the magnetic field. A nucleus has a maximum observable component of angular momentum $I(h/2\pi)$ when I, the spin quantum number, is finite. The angular momentum can be resolved into $2I + 1$ components which, because the angular momentum and nuclear moment (μ) behave as parallel vectors, necessitates the latter also having $2I + 1$ values and the nucleus the same number of energy levels. The frequency, ν_0, corresponding to transitions between these orientations is related to the field strength by the equation

$$\nu_0 = \mu H_0/Ih \tag{1}$$

where h is Planck's constant. It is the fact that the field strength observed by a particular nucleus may be different from the applied field, depending upon the chemical and physical environment of the nucleus, which makes nuclear magnetic resonance (n.m.r.) spectroscopy a tool of such immense importance for the study of liquid or gaseous samples in structural chemistry. Because each set of identical nuclei will respond at a slightly different applied magnetic field, each molecular species will give rise to a spectrum which usually permits its ready identification, alone or mixed with other molecular species of a different nature. No problem arises from overlap of the absorption regions of nuclei of different elements, or even from isotopes of the same element, which are well separated in the frequency spectrum.

Because the magnetic field, H_0, at a given nucleus depends upon its environment, the field may be represented by the equation

$$H_0 = H(1 - \sigma) \tag{2}$$

where H is the applied static field, and σ represents the factor by which this field is modified by the environment of the nucleus. The displacement of a resonance signal for different chemical environments caused by variations in the value of σ is referred to as a chemical shift (δ). Because of the way in which it is usually measured, the chemical shift is best expressed in terms of frequency:

$$\delta = (\Delta\nu/\nu_0)10^6 \tag{3}$$

where $\Delta\nu$ is the separation in c/sec between the sample and reference peaks, and ν_0 is the rf oscillator frequency in c/sec. Chemical shifts are usually given relative to a standard substance, and for protons this is often tetramethylsilane (TMS), although other substances have been used. For most protons δ lies in the range 0–15 ppm, which for an oscillator frequency of 100 Mc/sec, corresponds to 1500 c/sec. Much higher values of the chemical shift have, however, been observed in special situations. When TMS is used as a standard, negative values of δ are found for most protons. To avoid this difficulty Tiers has proposed an arbitrary scale,

$$\tau = 10 + \delta \tag{4}$$

which gives positive values in the majority of cases. The Tiers scale has been widely used, although, because the chemical shift is measured by the operator in c/sec, there is an advantage in the more direct δ-scale, in spite of the negative values.

Another important feature of n.m.r. spectra is the fine structure arising from a field-independent interaction which occurs between closely neighbouring nuclear spins. This interaction, known as spin-spin coupling, gives rise to splitting of the resonance line, and leads to spin-spin multiplets. Very detailed information about the environment of the nucleus in question may, in suitable cases, be obtained from a study of the distribution of the lines and of their intensities within the multiplet.

With solid samples the n.m.r. lines are broadened as a result of dipole–dipole[1] and electric quadrupole[2] interactions, and only wide lines devoid of fine structure are obtained. Application of this wide-line spectroscopy to analytical problems will be described later. With gases and liquids these interactions are averaged to zero as a consequence of the rapid tumbling motion of the molecules, and detailed fine structure is observed. It is in this high-resolution spectroscopy that the bulk of the chemical applications are to be found.

The potential of the technique as a qualitative tool for the identification of molecular species is now clear. When quantitative information is sought, other considerations arise. Because an n.m.r. signal will only be observed if there is an excess of nuclei in the lower energy state, the processes by which excited nuclei return to the ground state are of importance for the maintenance of the signal. If these relaxation processes are inefficient, the populations in the two energy states may become equalised, and the absorption signal will then disappear. This phenomenon is known as saturation. Two ways in which the nucleus may relax can be recognised. The energy may be transferred to the molecular system or lattice as translational or rotational energy. This mechanism is referred to as spin–lattice or longitudinal relaxation, and is characterised by a half-life or relaxation time T_1. In liquids and gases T_1 is short ($10^{-2} - 10^2$ sec); in solids T_1 may be measurable in hours or days. In a different relaxation process the spin energy may be exchanged with neighbouring nuclei. This is spin–spin or transverse relaxation, characterised by a half-life T_2. Spin–spin relaxation does not alter the distribution of the nuclei in the two spin states, but it does contribute to the line width of the resonance signal.

The mean life, Δt, of a nucleus in a given energy state determines the mean spread, ΔE_s, of the energy state, and is intimately related to the line width through the Heisenberg uncertainty principle,

$$\Delta E_s \,.\, \Delta t \approx h/2\pi \tag{5}$$

Because $\Delta E_s = h \,.\, \Delta \nu$, this implies that the uncertainty in the frequency of absorption

$$\Delta \nu \approx 1/2\pi\Delta t \tag{6}$$

The commonest broadening of resonance lines is that provided by the relaxation processes mentioned above. Strong interactions give rise to short relaxation times, and thus to wide lines. The magnetic field inhomogeneity can also contribute to the measured line spread.

The signal observed at the receiver coil of an n.m.r. spectrometer consists of two components, one in phase with the applied rf field, H_1, called the dispersion mode (u), and an absorption component (v) which is out of phase, the two components being readily separable by electronic phase-sensitive detection methods. The amplitudes of these signals are given by the expressions:

$$u = \frac{M_0\gamma H_1 T_2{}^2(\omega_0 - \omega)}{1 + (\gamma H_1)^2 T_1 T_2 + (\omega_0 - \omega)^2 T_2{}^2} \tag{7}$$

$$v = -\frac{M_0\gamma H_1 T_2}{1 + (\gamma H_1)^2 T_1 T_2 + (\omega_0 - \omega)^2 T_2{}^2} \tag{8}$$

where M_0, the total nuclear magnetic moment, is proportional to the number of magnetic nuclei present, and $\omega_0 - \omega$ is the distance from resonance in angular frequency units. Two features of these relationships are of importance in quantitative analysis. Although at first sight the dispersion mode may seem more useful because of its independence of T_1 and T_2 in certain circumstances, the fact that it falls off with $1/(\omega_0 - \omega)$, as against $1/(\omega_0 - \omega)^2$ for the absorption mode, makes the latter much more suitable for analytical purposes, because the broader dispersion mode signals may overlap in complex spectra. Secondly, the amplitude of these signals is a function of the relaxation times T_1 and T_2. Because these relaxation times may vary from one nucleus to another, even within the same molecule, the maximum amplitudes or peak heights are not necessarily a measure of the number of nuclei present.

A study of the integral of the absorption mode against time, assuming a linear sweep of the magnetic field at a uniform rate, dH/dt, reveals a more interesting situation, as shown by the equation

$$\int v \, \mathrm{d}t = \frac{\text{constant } NH_1}{T(\mathrm{d}H/\mathrm{d}t)[1 + (\gamma H_1)^2 T_1 T_2]^{1/2}} \tag{9}$$

in which N is the number of magnetic nuclei and T is the absolute temperature, the polarisation moment, M_0, being inversely proportional to T. Provided that T_1 and T_2 are short, or that the applied rf field is kept small, so that $(\gamma H_1)^2 T_1 T_2 \ll 1$, the integrated area will be independent of the relaxation times for the slow passage through the resonance signal for which the above equations are valid. It can be shown experimentally that if the rf driving field is kept sufficiently low, the area obtained will approximate closely to the true area, provided that the integrator can follow the rapid oscillations or "wiggles" of the oscillatory signal obtained when the rate of traverse of the field is insufficiently slow. There is no simple way in which the allowable rf level may be decided upon in advance. In practice the operator will wish to use a value of H_1 as high as possible to maximise the signal-to-noise level, particularly with dilute solutions, and it will then be necessary to run the spectrum at several increasing power levels to ensure that the maximum permitted value has not been exceeded. The important point to note is that if the rf power is properly chosen, the integral obtained will be closely proportional (within $\sim 1\%$) to the number of nuclei responsible for the observed signal.

Because, in the majority of cases, quantitative determination of the numbers of nuclei will be made by direct comparison in a single sample, or in a single molecular species, the fact that the integral is dependent upon temperature [equation (9)] will not affect the accuracy of the estimation unless the temperature were to vary rapidly during the course of the measurement. When the temperature is deliberately varied, as in a kinetic study, this dependence upon temperature must, however, be recognised, and allowance must be made for it.

The requirements of quantitative analysis clearly place severe demands on the frequency and magnetic field stability of the n.m.r. spectrometer and on the linearity of the detectors and amplifiers used in the recording and integration of the signal. It will be sufficient to say that commercial instruments are now readily available in which these requirements are satisfactorily met.

A further point should be noted. The signal strength in the receiver coil of the spectrometer theoretically depends upon the square of the magnetic field strength. It is, therefore, essential, where sensitivity is important, to work at the highest possible magnetic field and rf frequency. Much of the published quantitative work in n.m.r. has been carried out at an operating frequency for protons of 40 Mc/sec or 60 Mc/sec. However, commercial spectrometers operating at 100 Mc/sec and capable of meeting the requirements of quantitative analysis are now available, and offer substantial improvements in sensitivity. An additional advantage of a higher operating frequency in the field of analysis lies in the increased resolving power, because chemical shifts are field dependent and therefore proportional to frequency. This increased separation of the absorptions, which may be of critical importance in structural work, is also of considerable significance in quantitative analysis in so far as signals which overlap at a lower operating frequency may be sufficiently resolved to permit separate integration and evaluation.

On the debit side it should be mentioned that spectra obtained with spectrometers operating at around 100 Mc/sec may show fewer lines than are observed in spectra obtained from spectrometers operating at lower frequencies. These additional peaks are attributable to second-order splitting, and arise from electron-coupled spin–spin interaction between nuclei which are not first neighbours. The second-order separation is proportional to J^2/δ, where J, the spin–spin coupling constant, and δ, the appropriate chemical shift, are both expressed in c/sec. Because J is a constant for a given molecule and δ is field-dependent, the second-order separation, easily observable at low field strengths, gradually disappears within the natural line width as the applied field is increased in strength. It has been pointed out,[3] however, that almost all of the chemically valuable information, except relative signs of coupling constants, is available by direct measurement of the chemical shifts and spin–spin splittings in the *first order* spectrum, and the second order structure can be computed, if desired, from these parameters.

(*B*) *Experimental method*

The basic n.m.r. spectrometer consists of a large magnet, providing a stable and very homogeneous magnetic field, an rf oscillator, a single coil or crossed coil system containing the sample and located between the pole pieces, and a sensitive receiver. For analytical purposes the important features required are sensitivity, stability and reproducibility. The most useful recent advances have been in systems designed to maintain the stability of the applied magnetic field and to provide electronic integration of the n.m.r. spectrum. Some commercial spectrometers employ flux-stabilisers in which special windings on the pole pieces develop voltages proportional to the rate of change in magnetic flux intensity. These voltages are used, after amplification, to produce suitable corrections to the applied field. Such stabilisers, in conjunction with carefully regulated power supplies, provide magnetic fields of very high stability. Other spectrometers employ a system in which a nuclear resonance signal is employed to maintain a definite relationship between the applied magnetic field and the oscillator frequency rather than to maintain a specified magnetic field. These systems, employing a field-frequency locking system, are particularly advantageous from the point of view of reproducibility, and may be used for rapid routine measurements with the minimum of attention to the spectrometer controls. N.m.r. spectrometers incorporating facilities for electronic integration of the spectrum have been commercially available for some time. Reproducibility and accuracy in integration are dependent on many factors, including signal-to-noise ratio, line width, and variations in sample temperature. With available circuits and chart recorders, a reproducibility to 1% can be expected under good conditions. This accuracy may be improved by averaging a number of such integrations, and where the maximum accuracy is required the output of the integrator may be applied simultaneously to a digital voltmeter. Jungnickel and Forbes[4] have shown that under optimum conditions of sample concentration, rf power, gain and sweep rate, integrals should be accurate to within a few tenths of 1% of the total hydrogen content. The sensitivity depends upon a number of factors, including, as has been indicated already, the rf oscillator frequency. At 100 Mc/sec, identification may be made with as little as 0·1–0·2 mg of sample in a suitable cell, whilst useful quantitative results may often be obtained with about ten times this quantity of material. At lower frequencies, higher concentrations of solutions are necessary. Much of the published results have been obtained at 60 Mc/sec using solutions of 5–20% concentration and a sample volume of about 0·5 ml.

(*C*) *Applications of high-resolution n.m.r.*

(*i*) *Proton resonances: General.* The proton is by far the most important nucleus for study by high-resolution n.m.r. spectroscopy. It gives a stronger resonance signal than any other nucleus of chemical interest, and the spectra are not complicated by quadrupole relaxation effects present in the spectra of nuclei with spin greater than 1/2. The chief disadvantage in proton spectroscopy is the smallness of the chemical shifts, which are, in general, more than an order of magnitude smaller than in other n.m.r. spectra. Although proton resonance lines are usually sharp except when molecular motion is restricted, the small range of chemical shifts often prevents complete resolution of the lines, especially with spectrometers operating at 60 Mc/sec and under. Accordingly, both the experimental measurements and their interpretation are made more difficult.

High-resolution proton spectra are used most frequently for the determination of the structure of hydrogen-containing molecules. Although the consideration of n.m.r. as a structure-determining tool is outside the scope of this review, it may be noted that the use of high-resolution spectra in solving problems in structural organic chemistry is well advanced. A procedure for extracting the structure information made available by the n.m.r. technique is described by Chamberlain.[5] Useful correlations of proton chemical shifts with chemical structure have been published as charts[6] and as tables.[7,8]

(*ii*) *Qualitative analysis.* The use of high-resolution n.m.r. as a qualitative analytical tool is now firmly established. For each compound the n.m.r. spectrum is probably unique. The number and relative intensities of the resonances, their chemical shifts and multiplicities from spin–spin coupling, and also their relaxation times, allow such a vast number of possibilities that it is most unlikely that two different chemical compounds would have the same n.m.r. spectrum. Although, in general, it is desirable to unravel the n.m.r. spectrum of a complex molecule and express it in terms of chemical shifts and spin–spin coupling parameters before attempting to draw conclusions concerning the molecular structure of the sample, it is frequently possible to identify unknown compounds of considerable complexity by simple inspection of the n.m.r. spectra and comparison with the spectra of known molecules. Consequently, the publication of classified high-resolution spectra, already begun for hydrogen-containing molecules,[9] should eventually make the "fingerprinting" of molecules by their n.m.r. spectra very attractive.

The chemical shift is used analytically as the primary means of identification of functional groups containing the observed isotope. Notwithstanding the small range of proton chemical shifts, it is often possible in mixtures of hydrogen-containing compounds to select a peak as being representative of a given compound in the mixture. Detection of the compound then requires a simple examination of the proton spectrum for this peak. A good example of this type of application is the detection of specific compounds, such as benzene in such a complex mixture as aviation fuel.[10] Where doubt exists as to the identity of signals, it is usual to run the spectrum and then add some of the compound in question, noting whether or not the appropriate peaks increase in amplitude, or whether additional peaks appear in the spectrum. Because the observed resonance signal may arise from a very small percentage of the hydrogen in a given compound, the sensitivity of the n.m.r. method in applications of this kind will not always be large, but in favourable cases high sensitivity can be achieved.[11]

(*iii*) *Proton counting.* The number of hydrogen atoms of each type in a molecule can readily be obtained by high-resolution n.m.r. spectroscopy using integrated spectra. This is illustrated in Fig. 1 which shows both the absorption and integrated spectrum for prodigiosin[12] obtained at 60 Mc/sec. From the value of the chemical shift it seems certain that the peak at −235 c/sec represents the three protons of a methoxyl group. The integral of the remaining protons then gives 22, making a total of 25 for the molecule. For molecular structure determination, proton counting by n.m.r. has the great advantage that it allows the number to be fixed to the nearest proton. Calculations made solely from molecular weight determinations and hydrogen analyses are often accurate only within several hydrogen atoms. The n.m.r. method requires that at least one peak be positively identified. If this is not possible, an approximate molecular weight and percentage of hydrogen will serve to fix the total number of protons, because each step on the integral curve should represent an integral number of protons and often approaches closely to such a value.

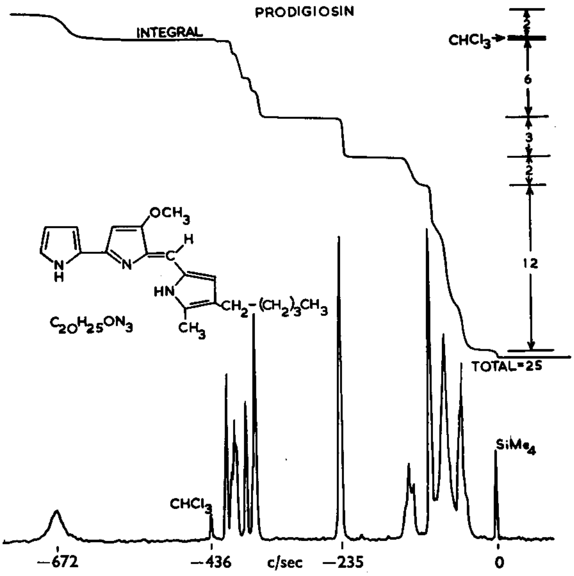


FIG. 1.—Proton counting as demonstrated on the molecule prodigiosin (Varian Associates[12]).

(*iv*) *Total hydrogen analysis.* Another application of integrated n.m.r. intensities lies in the analysis of small samples for total hydrogen. By comparison with compounds of known hydrogen content in sample tubes of identical cross-sectional area, it is possible to determine the percentage of hydrogen by weight in an unknown sample. Table I shows the results obtained for three complex natural products with naphthalene used as a standard.[13] The naphthalene was run in triplicate to establish the precision of the measurement. The percentage of hydrogen by weight agrees in

TABLE I.—TOTAL HYDROGEN ANALYSIS BY N.M.R. FOR COMPLEX ORGANIC MOLECULES[13]

Sample	Wt., *mg*	H, % (by wt.)	H, % (n.m.r.)[a]
$C_{10}H_8$ (A)	25·1	6·29	6·31 ± 0·03[b]
$C_{10}H_8$ (B)	25·3	6·29	6·28 ± 0·01
$C_{10}H_8$ (C)	25·3	6·29	6·28 ± 0·02
$C_{27}H_{44}O_3$	25·1	10·65	10·58 ± 0·05
$C_{15}H_{18}O_6$	25·2	6·26	6·27 ± 0·04
$C_{15}H_{20}O_6$	25·1	6·80	6·81 ± 0·03

[a] Based on average integral of naphthalene solutions
[b] Standard deviation

nearly all cases with calculated values to within the standard deviation of the measurement, which is about 0·5% of the percentage present. This accuracy compares favourably with the standard combustion method. The accuracy, speed and non-destructive nature of the n.m.r. analysis may make the method more attractive than the combustion method when a limited amount of sample is available.

(*v*) *Quantitative analysis of mixtures.* The capability of obtaining accurate integrals has greatly extended the analytical usefulness of the high-resolution n.m.r. spectrometer and permitted its application to many other important problems. Thus, the addition of electronic integrators has made possible the complete quantitative determination of the components in an increasing variety of mixtures. One recent example of this type of analysis has been described by Hollis.[14] Considerable effort has been devoted to the problem of developing suitable methods for the routine quantitative analysis of commercial analgesic preparations containing aspirin, phenacetin and caffeine. Procedures have been published utilising separation by extraction and partition chromatography, and determination by ultraviolet, visible and infrared spectrophotometry. The extraction procedure is not suitable for routine quality control because of the time required to complete the analysis. Of the other procedures the infrared method seems to be most advantageous in terms of accuracy and speed. The accuracy and speed of the n.m.r. method described by Hollis is about the same as that of the infrared procedure, but it has the advantages of being more direct, in that a separate analytical peak of known origin is present for each component and no calibration curves are required. The results obtained by n.m.r. show that the technique can be used to analyse commercial aspirin-phenacetin-caffeine preparations with an accuracy sufficient for quality control purposes.

Chupp and Speziale[15] have used the n.m.r. method to advantage in a study of the *N*-hydroxymethylation of some *N*-methylamides by formaldehyde. Assay of the reaction mixtures by titration of excess formaldehyde is open to criticism because of the possibility that only formaldehyde is titrated and the doubt whether the equilibrium is stable under conditions of varying pH. The authors successfully used 60 Mc/sec spectra with electronic integration to obtain quantitative estimates of the reactants, products and unchanged formaldehyde in a large number of different reaction systems. Conventional chemical analysis by isolation of crystalline derivatives presents serious difficulties in this kind of mixture.

(*vi*) *Characterisation of mixtures.* Many multicomponent systems are so complex that the complete determination of their composition is extremely difficult. In such cases a great deal of valuable information can still be obtained from a knowledge of the functional groups present and their quantitative distribution. This characterisation leads to a knowledge of the compound types present and sometimes permits the deduction of a structure for the "average molecule". Williams[16] [see also ref. (5) p. 1935] has presented analytical schemes for characterising saturated, aromatic and olefinic fractions derived from petroleum, based upon high-resolution n.m.r. measurements giving the hydrogen distribution, total hydrogen content and average molecular weight. These characterisations have proved very helpful in following the processing of petroleum fractions.

(*vii*) *Molecular weight determination.* The determination of molecular weights by n.m.r. again involves comparison of the integrated intensities of an added standard and of a recognisable peak or group of peaks of the unknown in a solution containing known weights of standard and unknown. The molecular weight is given by the formula:

$$M = \frac{I_s n W M_s}{I n_s W_s} \tag{10}$$

where I = intensity, n = number of protons in the peak or peaks, W = weight and M = molecular weight (subscript s = standard). Barcza[17] found that a suitable standard is hexamethylcyclotrisiloxane, removable by sublimation. Other possible standards include iodoform, benzoquinone and, in the absence of complex formation with aromatic unknowns, *p*-dinitrobenzene and 1,3,5-trinitrobenzene. The molecular weight determination can be combined with taking the n.m.r. spectrum of the unknown, the only extra work required being the weighing of sample and standard, and the calculation. Important features of the n.m.r. method are that the molecular weight values obtained in this way are not affected by dissociation and solvent interaction phenomena, and the error resulting from impurities is proportional to their weight. On the assumption that most impurities are smaller molecules than the unknown, this method should, therefore, give smaller errors than methods depending primarily on the number of particles present. Possible sources of error in the measurement, and details of procedure, are discussed by Barcza.[17] As pointed out by this author, the protons of hydroxyl groups exchange with moisture in the solvent, hence absorption peaks attributable to these protons should not be used in the determination.

Both the unsaturation and the average molecular weight of fatty acid triglycerides (natural fats) have been estimated by Johnson and Shoolery[18] using the n.m.r. technique. The proton spectra of these triglycerides in carbon tetrachloride were characterised by the signals from the olefinic protons, the four glyceride methylene protons, methylene groups attached to two doubly-bonded carbon atoms and the protons on saturated carbon atoms. By using the area of the signals from the C_1 and C_3 glyceride protons as an internal standard, the number of olefinic protons and the total number of hydrogen atoms can be determined. From these determinations the average molecular weight can be calculated. An iodine number obtained from the number of olefinic protons and the average molecular weight agrees well with that determined by the Wijs titration method. The total time spent in obtaining the n.m.r. results was about 20 min per sample. The calculation can be simplified by using suitable nomographs.

(*viii*) *Polymer analysis.* Few articles have appeared in the literature on the application of high-resolution n.m.r. to the study of polymers. This situation may have arisen because few polymers have a high enough solubility and at the same time exhibit narrow enough line widths to permit a detailed analysis of their spectra with the spectrometers available until quite recently. With the advent of more sensitive spectrometers, the position is changing rapidly and it seems likely that high-resolution n.m.r. spectroscopy will also prove of increasing importance in this field of study. A general discussion of the application of high-resolution n.m.r. to the study of polymers has been given by Bovey, Tiers and Filipovich.[19] These authors point out that the line widths obtained in n.m.r. spectra of polymer solutions are dependent on the local viscosity in the immediate neighbourhood of the chain segments and not on the macroscopic viscosity of the sample. The local viscosity is independent of molecular weight and is influenced by concentration only when this becomes so high that segmental motion is restricted. These observations are utilised in the determination of stereochemical configurations and functional groups in polymeric systems. An example of the former is the determination of the relative amounts of iso-, syndio- and atactic triads in methyl methacrylate polymers by measurement of proton peak areas in the α-methyl region of the spectrum.[20] Chen[21] has used high-resolution n.m.r. to determine the structural groups in butadiene-isoprene copolymers of varying composition and in the molecular weight range of 100,000 to 200,000. These copolymers gave well-resolved spectra in carbon tetrachloride solution at room temperature. The error in determining the relative concentrations of the various structural groups in a typical 1:1 butadiene-isoprene copolymer was estimated to be within 2–3%.

Infrared procedures have been widely used for the determination of the microstructure of polyisoprene. The method is satisfactory for the determination of the 1,2- and 3,4- repeating units, but is unsatisfactory for the determination of the *cis*- and *trans*-1,4- unit contents of polyisoprenes.[22] It has now been shown[22] that the areas of the *cis*- and *trans*-methyl n.m.r. peaks in solutions of 1,4-polyisoprene are satisfactory measures (estimated error ±0·5%) of the *cis*- *trans* content of the polymer. In combination with the n.m.r. method previously described by Chen,[21] this analysis can be extended to polyisoprenes containing *cis*- and *trans*-1,4-, 1,2- and 3,4-recurring units with an over-all error of 2–3%.

Senn[23] has developed a method for the analysis of styrene-butadiene copolymers using the n.m.r. absorption bands derived from the aromatic and olefinic protons incorporated into the copolymer. The composition of the copolymer is determined in terms of the mole per cent styrene, 1,2-butadiene addition and 1,4-butadiene addition, and no calibration is required. The major time-consuming step in the method, which has been used routinely for determining styrene-butadiaene copolymer composition, is the dissolution of the sample. The time required for analysis after dissolution is approximately 20 min.

The detection and estimation of branching in polymers has always been a difficult problem because of the absence of a convenient physical method of analysis. It has now been shown that n.m.r. spectroscopy can be used not only to detect branching in dextran, but also to make a reasonably good estimate of the extent of branching.[24] The proton spectrum of branched dextran contains a peak, not found in the spectrum of linear dextran, which is assigned to C-1 protons at non-1,6-linkages, linkages which in most branched dextrans form the branch points. A quantitative measure of the extent of branching, the ratio of 1,6-linkages to non-1,6-linkages, is thus obtained by taking the ratio of the areas of the peaks associated with these two types of linkage. The ratio so obtained (71:29) agrees well with that obtained by periodate analysis (70:30). This method of detecting and estimating branching can obviously be extended to other polysaccharides in which the non-1,6-linkages are known to be at branch points. In principle the method should be applicable to polymers other than polysaccharides.

(*ix*) *Analysis of surfactants.* Previous methods of characterisation of non-ionic surfactants containing a polyoxyethylene chain have been slow and rather inaccurate. Quantitative measurement of the proton signal intensity in high-resolution n.m.r. spectra offers a simple and relatively rapid method (a complete determination can be made in about 30 min) for determining the composition and structure of such materials.[25] Relative amounts of protons are determined to characterise the hydrophobe and to find the ratio of the hydrophilic to hydrophobic portions of the molecule. When applied to alkyl phenol-ethylene oxide condensates, the method allows the average molecular weight of each portion of the molecule to be determined directly. The authors discuss the applicability of the method to the characterisation of other common commercial non-ionic surfactants. All represent cases where standards, other than a known portion of the molecule, are unnecessary for quantitative measurements.

(*x*) *Isotope analysis.* Isotope-abundance ratios are readily obtained by the n.m.r. method. Thus, proton resonance has been used to measure the water content of H_2O–D_2O mixtures with an accuracy of $\pm 0{\cdot}2\%$, the analysis being completed in a few minutes by comparison with standards of known concentration.[26] Mitchell and Phillips[27] have applied the proton n.m.r. technique to the measurement of H_2O in D_2O in a flowing sample, using a special sample tube arrangement. When only small amounts of H_2O are to be detected, a dilution technique gives increased sensitivity.[28] Known amounts of H_2O are added to accurately measured aliquots of the H_2O–D_2O sample. The amplitude of the proton signal is measured and plotted against the amount of H_2O added. Extrapolation of the plot to zero signal amplitude enables the concentration of H_2O in the original sample to be obtained from the intercept on the concentration axis.

Whether or not deuterium enters an organic compound (by exchange with protons) and where it has been substituted for hydrogen are analytical problems which can be rapidly solved by high-resolution n.m.r. spectroscopy. Organic applications involving deuterium so far reported have all been in terms of the influence of deuterium substitution upon the proton spectrum. Thus, proton n.m.r. has been used to establish the deuteration sites and to determine the degree of deuteration in

$$C_6H_5\,CD\,(CHD_2)\,CHD\,CHD\,CO_2H.^{29}$$

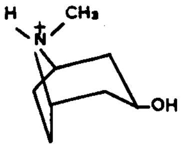
Similarly, proton spectroscopy has been used to measure the amount of ^{13}C enrichment in a methyl group with an accuracy of $\pm 0{\cdot}1\%$.[30]

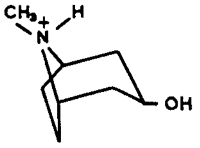
(*xi*) *Estimation of hydration numbers.* Nuclear resonance studies have provided information on ion hydration. Zhernovoi and Yakovlev[31] have measured the proton relaxation time, T_1, in water and in the dihydrogen phosphate ion, using aqueous solutions of sodium dihydrogen phosphate and of potassium dihydrogen phosphate. Their results can be explained by assuming positive hydration for ions like sodium and negative hydration for ions like potassium. A study of the ^{17}O resonance in water enriched in ^{17}O (abundance $0{\cdot}096\%$) has indicated that solvent water can be distinguished from water in the hydration sphere of certain cations. Jackson, Lemons and Taube[32] found that for aquo-cations with a slow rate of water exchange (half-life $> 10^{-4}$ sec) it is possible to display the hydration water as a separate n.m.r. peak when the solvent peak is shifted by addition of a paramagnetic ion. The actual ^{17}O shift observed will depend on the number of water molecules involved in the aquo-cation, and thus not available to interact with the paramagnetic ion. The authors suggest either the measurement of the relative areas under the absorption curves of solvent water and bound water or a method based on the effective molal shift of solvent water for the estimation of hydration numbers. Unfortunately, the enrichment level of the ^{17}O at present available does not permit precise determination of these numbers.

(*xii*) *Determination of sample purity.* An important use for high-resolution n.m.r. spectroscopy is the determination of the purity of a given sample. As the example[33] given below illustrates, the n.m.r. method compares favourably with more conventional methods or criteria for determining the homogeneity or otherwise of a sample. Supposedly pure 5,16-pregnadiene-3β,20α-diol, obtained by lithium aluminium hydride reduction of 16-dehydropregnenolone acetate, resisted separation into two components by thin-layer, paper, gas-phase and conventional column chromatographic techniques. Inspection of the n.m.r. spectrum showed that in the region of the spectrum where one would expect a singlet associated with the absorption produced by the C-28 methyl protons there occurred two peaks separated by 3 c/sec, each with one half the intensity of the single C-19 methyl resonance. Furthermore, the doublet associated with the C-21 methyl group appeared as a discrete pair of doublets. The author concluded that the supposedly pure 20α-hydroxy compound was, in fact, a molecular complex of the epimeric 20α- and 20β-diols.

(*xiii*) *Applications to the study of equilibria and kinetics.* The non-destructive nature of the n.m.r. method, and the selective character of high-resolution spectra, make the technique particularly valuable for the study of equilibria and of rate processes in solution. In these situations the n.m.r. method may have marked advantages over other physical or chemical analytical techniques, although some problems remain. Because of the requirement of a spinning sample to obtain the necessary field homogeneity in high-resolution studies, temperature control is less simple than in some other techniques. Grunwald, Loewenstein and Meiboom,[34] in an early rate study, relied on temperature control of the room, which remained within $\pm 2°$ over a period of days. The problem of temperature control of the sample has now largely been solved, and devices using a rapid flow of preheated or precooled nitrogen, and capable of maintaining any temperature within the range $-60°$ to $+200°$, are commercially available. Again, in some equilibrium studies, the $\pm 1\%$ accuracy obtainable in ordinary circumstances may be insufficient. Solubility limitations may also operate.

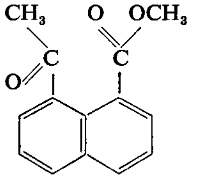
The advantages of the technique are illustrated by studies of the keto-enol tautomerism of acetylacetone (2,4-pentanedione).[35] At 40 Mc/sec the signals from the tautomers are well separated, and the relative areas under the $-CH_2-$ and $=CH-$ peaks have been used to obtain the relative concentrations of the keto and enol forms. An earlier investigation,[36] in which bromine titrations were used in the analysis, gave a considerably higher proportion of the keto tautomer, but there is no reason to doubt the accuracy of the n.m.r. results. The effect of temperature on this equilibrium has been examined.[37] Closs[38] has studied the equilibrium, in acid solution, between the isomeric forms of pseudo-tropine hydrochloride which arise





from the two possible configurations of the *N*-methyl group. The CH_3 resonance appears as a doublet in each case, consequent on splitting produced by the adjacent hydrogen nucleus, and the relative amounts of each isomer were estimated by measuring the areas under the respective doublets by cutting out from the chart the peak areas and weighing. Using a series of ten estimations the error in the area estimation was believed by these investigators to be ±10%. Much higher accuracy could doubtless have been obtained by electronic integration. In D_2O the CH_3 doublets collapse to a singlet as the hydrogen nucleus is replaced by deuterium, and better estimation of the areas is possible. Although of limited accuracy, this study is an excellent example of the ease with which the separate determination of molecular species differing in structure only in a most subtle way may be effected by the n.m.r. method.

Lansbury and Bieron[39] have used the n.m.r. technique to investigate the keto acid–pseudo acid tautomerism in the normal- (I) and Ψ-methyl esters (II) of 8-acetyl-1-naphthoic acid



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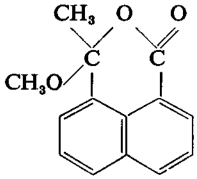

II

One of the methyl signals in I is typical of a methyl aryl ketone, whereas in the Ψ-ester it is typical of a methyl ether. Quantitative analysis of the mixture was effected by electronic integration of the 60-Mc/sec spectrum with an estimated accuracy of ±1%. This analytical procedure was checked by a study of synthetic compositions.

Rearrangement of 3,3-dichloro-*exo*-tricyclo [3.2.1.0] octane (III) to *exo*-3,4-dichlorobicyclo [3.2.1] oct-2-ene (IV) was easily followed by De Selms and Combs[40] by observing the disappearance of the absorption of III at 9·24τ from one of the protons on carbon-8 and the simultaneous appearance of the absorptions of IV at 3·92τ and 5·89τ because of the protons on carbon-2 and carbon-4. The rearrangement exhibited first-order kinetics at 22° in carbon tetrachloride and a number of other solvents.

Clearly, therefore, there is a wide field of application in which n.m.r can be used as an analytical technique of unrivalled discriminating power for measuring the relative amounts of reacting species, either in equilibrium systems or in the course of slow reactions, that is to say, reactions which are slow relative to the time required to obtain a high resolution spectrum, which is usually of the order of several minutes. Faster reactions may be studied by an entirely different n.m.r. method which permits the measurement of rate processes with half-lives in the approximate range 0·002–0·2 sec. Where exchange of a nucleus between two separate species occurs in a molecular system, the nature of the spectrum obtained depends on the magnitude of the rate of exchange of the nuclei. If exchange is slow, the spectrum will consist of two separate but superimposed spectra corresponding to the two individual species. With sufficiently fast exchange a time averaged spectrum will be observed. In intermediate cases predictable line shapes are observed, and from a study of the detailed line shape information may be obtained about the rate of exchange. Similarly, multiplets caused by coupling with a nucleus which is exchanging rapidly will merge to a single line if the frequency of exchange is large compared with the spin–spin coupling. In general, therefore, information may be obtained by this method in cases where the frequency of exchange is comparable with the frequency separation in the spectrum.

The theory of this averaging effect has been discussed by Gutowsky and his coworkers.[41] The effect has been demonstrated for the hydroxyl protons of ethanol by Arnold.[42] Grunwald, Loewenstein and Meiboom have used it with advantage to study the protolysis of methylammonium ions in aqueous solution.[34] The exchange rate is nearly proportional to $[CH_3NH_3^+][CH_3NH_2]$, the second-order rate constant being $6 \times 10^8\,M^{-1}\,.\,\mathrm{sec}^{-1}$ at 19°. Two separate reactions appear to contribute to this rate constant, one being the direct transfer of a proton from $CH_3NH_3^+$ to CH_3NH_2. The other, it is clear from the broadening of the water line and from the merging of the H_2O and NH_3^+ resonances into a single line at higher pH values, involves a solvent molecule. This investigation is an example of the large amount of quantitative information obtainable from the n.m.r. spectra. Similar studies of the dimethyl- and trimethylammonium ions have been described by Loewenstein and Meiboom.[43] From an examination of line-broadening, information has been obtained about the proton exchange rate between t-butanol and some alkynes, $R—C \equiv CH$, in aqueous solution.[44] The exchange is catalysed by hydroxyl ions, and the rate-determining step is believed to be the removal of the terminal acetylenic protons by the hydroxyl ion.

In the method just described a limit is imposed by the resolution of the spectrometer, there being a finite contribution to the measured line width from the inhomogeneity of the applied magnetic field. Forsen and Hoffman[45] have described a different method which does not depend on the line widths and separations in a single resonance spectrum. Consider a simple two-component system in which a nucleus is rapidly transferred back and forth between two non-equivalent sites A and B. In a double resonance experiment, when the signal from the nucleus at site B is saturated by a strong rf field, and the signal from site A is simultaneously observed by a weak field, its decay to zero may be followed as a function of time (t). It can be shown that M_z^{A}, the z-axis magnetisation at site A, is given by

$$M_z^{\mathrm{A}} = M_0^{\mathrm{A}} \left[\frac{\tau_{1\mathrm{A}}}{\tau_{\mathrm{A}}}\,.\,\exp.\left(-\frac{t}{\tau_{1\mathrm{A}}}\right) + \frac{\tau_{1\mathrm{A}}}{T_{1\mathrm{A}}}\right] \tag{11}$$

where M_0^{A} is the initial z-magnetisation at site A, τ_{A} is the lifetime of the nucleus in site A, $T_{1\mathrm{A}}$ is the spin-lattice relaxation time in site A, and $\tau_{1\mathrm{A}}$, the time constant obtainable from a logarithmic plot of the decay curve, is defined by

$$\frac{1}{\tau_{1\mathrm{A}}} = \frac{1}{T_{1\mathrm{A}}} + \frac{1}{\tau_{\mathrm{A}}} \tag{12}$$

From the value of $\tau_{1\mathrm{A}}$ and the quotient $\tau_{1\mathrm{A}}/T_{1\mathrm{A}}$, τ_{A} and $T_{1\mathrm{A}}$ may be obtained. From a second double-resonance experiment in which B is observed while A is saturated, τ_{B} and $T_{1\mathrm{B}}$ may also be evaluated. Thus, the lifetimes in the two states are separately obtained, as are the two spin-lattice relaxation times. The method has been applied to the exchange of the hydroxyl protons in an equimolar mixture of t-butanol and 2-hydroxyacetophenone. It clearly provides interesting information relevant to the exchange mechanism, as well as quantitative information on the rate process.

Where two rapidly exchanging kinds of proton contribute to the same n.m.r.

absorption line the observed chemical shift may be a linear function of the concentration ratio of the two species,[46–48] if the change in composition is not accompanied by gross changes in the solvent medium. This observation has been utilised by Grunwald Loewenstein and Meiboom[49] to study acid-base equilibria in systems containing trimethylammonium ions. The chemical shift follows the typical S-shaped titration curve when plotted against pH. Bhar and Forsling[50] have made use of the same phenomenon in a study of the kinetics of the hydrolysis of acetic anhydride to acetic acid. Similarly, the dimerisation constant for acetic acid in carbon tetrachloride has been obtained from a study of the chemical shift of the OH proton on dilution caused by the rupture of the hydrogen bonds in the dimer.[51]

(*xiv*) *Other nuclei.* References in the literature to analytical applications with nuclei other than ^{1}H and ^{19}F are severely limited. Several factors contribute to this situation, notably the much lower signal strength obtained with some nuclei which would otherwise be of considerable chemical and analytical interest. In others, with $I \geqslant 1$, the presence of an electric quadrupole moment leads to short relaxation times and excessive line broadening. Again, spin-lattice relaxation times may be unfavourably long. There is a compensating advantage, however, in that, because the chemical shifts are frequently much larger than in proton spectra, and the requirements in homogeneity therefore less stringent, much larger samples may be employed.

For a given magnetic field and a fixed number of magnetic nuclei the intensity of the n.m.r. absorption signal is proportional to

$$\frac{I+1}{I^2}\mu^3 H_0^2 \tag{13}$$

Values of the spin I in multiples of $h/2\pi$, magnetic moment μ in multiples of the nuclear magneton, and the relative sensitivity for a fixed number of nuclei are shown in Table II for a number of magnetic nuclei of interest from the analytical standpoint. ^{12}C and ^{16}O are non-magnetic. Of the nuclei with spin 1/2, other than the proton, ^{19}F in particular, and ^{31}P are clearly promising from the viewpoint of quantitative analysis. The low natural abundance (4·70%) of ^{29}Si, which also has a spin of 1/2, contributes to the difficulties in making full use of this isotope. Nuclei with $I \geqslant 1$, *i.e.*, ^{11}B, ^{14}N and ^{35}Cl, present difficulties because of the quadrupole relaxation effect, although in some cases, notably ^{11}B and ^{14}N, this has not prevented much useful structural information being obtained. In practice, quantitative analytical applications appear to have been confined to ^{1}H, ^{19}F and ^{31}P.

Muller and Goldenson,[52] in an early paper, described the application of ^{31}P measurements to the analysis of mixtures of phosphorus compounds. The spectra were obtained at 17 Mc/sec in a field of 9850 gauss, and areas rather than peak heights were used because of probable differences in relaxation times. Integration measurements made by a weighing technique on a series of six recordings led to an estimated accuracy in the analysis of 1–2%. In a later study Ames *et al.*[53] investigated the system H_2O–HF–P_2O_5 by ^{31}P resonance, and succeeded in estimating quantitatively the nine separate structural entities possible in this system. Proton spectra are of no value in this case because the rapid interchange of the acidic hydrogens of HF, the protons in water and in the various phosphoric acids leads to a single proton resonance line useless for analysis. Both ^{31}P and ^{19}F spectra were obtained with the same magnet at about 9000 gauss. The samples were contained in 15-mm o.d.

polyethylene tubes with a reference material (85% phosphoric acid for the ^{31}P spectra or 100% trifluoracetic acid for the ^{19}F spectra) contained in a small concentric tube. Spectra were obtained using the absorption mode, and the areas of the resulting resonance peaks were measured by weighing traces on a paper of uniform weight. Replicate ^{19}F area measurements showed a standard deviation of 2·4% of the peak area on peaks exhibiting areas in the range of 15–30% of the total fluorine, whereas replicate ^{31}P area measurements showed a standard deviation of 5·0% in the same range. The increased accuracy in the fluorine measurements arises partly from the improved signal-to-noise ratio at the higher fluorine resonance frequency and partly to the greater multiplicity of the spin–spin multiplets in the phosphorus spectra. Groenweghe and Payne[54] used a similar technique to investigate the mixed halide systems $POCl_3$–$POBr_3$ and $PSCl_3$–$PSBr_3$ using the ^{31}P resonances. Because of the large chemical shifts in these systems (~140 ppm), which meant that resonance peaks were observed at fields relatively far apart, the authors found it necessary to correct the results obtained by the weighing technique for deviations from linearity of the magnetic field sweep. Corrections up to 13% of the measured areas were applied. Van Wazer and Fluck,[55] in a subsequent paper from the same laboratory in which a study of the system H_3PO_4–$POCl_3$ was described, omitted the sweep non-linearity correction. A study of the system phosphorus trichloride, tribromide and triphenyl phosphite by the n.m.r. method has also been reported.[56] A detailed study of the application of ^{31}P resonances to the analysis of polyphosphoric acids has been described by Guffy and Miller.[57] Absorption mode spectra were used and area measurements were made with a planimeter. The total time required for an analysis was estimated to be 15 min, including setting up of probe balance (5–8 min), area measurements (4–6 min) and calculations (1–2 min). These authors found comparison of peak heights less satisfactory, and claimed an accuracy in the area measurements of ±2%. The area measurements gave the ratio of end-phosphorus groups to ortho-phosphorus groups from which the acid concentration could be calculated with an estimated accuracy of ±0·2%, checked by magnesium pyrophosphate determinations. Guffy and Miller claimed the method to be as accurate as the best wet methods available, and the sensitivity for showing slight differences in composition even better. It should be noted, however, that the method is not suitable for low

TABLE II.—NUCLEAR PROPERTIES*

Isotope	I	μ	Resonance frequency at 10 kgauss, *Mc*	Relative sensitivity at constant field
^{1}H	1/2	2·79268	42·576	1·000
^{2}H	1	0·85738	6·536	$9·64 \times 10^{-3}$
^{7}Li	3/2	3·2560	16·547	0·294
^{11}B	3/2	2·6880	13·660	0·165
^{13}C	1/2	0·70220	10·705	$1·59 \times 10^{-2}$
^{14}N	1	0·40358	3·076	$1·01 \times 10^{-3}$
^{17}O	5/2	−1·8930	5·772	$2·91 \times 10^{-2}$
^{19}F	1/2	2·6273	40·055	0·834
^{29}Si	1/2	−0·55477	8·458	$7·85 \times 10^{-2}$
^{31}P	1/2	1·1305	17·236	$6·64 \times 10^{-2}$
^{35}Cl	3/2	0·82091	4·172	$4·71 \times 10^{-3}$

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concentrations because of the unfavourable intensity of the resonance signals compared with proton or fluorine spectra. Fluorine resonance has been used in quantitative analysis of mixtures of uranium hexafluoride and bromine pentafluoride.[58]

(D) *Applications of wide-line n.m.r.*

Wide-line n.m.r. stands on the same theoretical foundation as the high-resolution technique, but the spectra obtained by the respective methods differ considerably. In wide-line measurements fine spectral details are not obtained; line widths and shapes, particularly as a function of temperature, are the features from which intelligence usually is derived. For this reason, the instrumentation in this type of spectroscopy is simpler than in the high-resolution method.

Wide-line n.m.r. provides a simple, rapid method for the quantitative measurement of isotope concentration in liquid samples. Of particular interest are the determination of light water in D_2O,[59] of residual hydrogen in highly fluorinated or deuterated compounds,[59] and of fluorine in fluorocarbon liquids.[60] Because of the relative size of the chemical shifts, differences exist between hydrogen and fluorine analysis by the wide-line technique. In proton resonance from liquids the shifts are too small to be detected with the magnet used in a broad-line instrument. In fluorine resonance the chemical shifts are larger by an order of magnitude, and can be observed with magnets of such homogeneity. Quantitative analysis of fluorine-containing organic molecules from integrated intensities can, therefore, lead to the determination of both the total fluorine content and fluorine present in different groups.[59] Other nuclei which have been examined in the liquid state by wide-line n.m.r. for quantitative analytical purposes[59] are ^{11}B and ^{27}Al.

One of the most important current applications of the wide-line technique involving quantitative analysis is the accurate and rapid determination of the water content in a wide variety of agricultural and food products.[61] The principle underlying this application is that the n.m.r. absorption is broadest in "rigid lattice" solids and that molecular motions result in line narrowing. Consequently, the proton resonance spectrum of the above systems consists of a narrow line arising from the moisture, superimposed on a broad line from the less mobile protons in the host material. Two procedures have been used for determining the moisture content. In one method, the peak-to-peak amplitude of the derivative of the absorption signal from the moisture is measured. This is then compared with a calibration curve for the material to be analysed, obtained under standardised conditions using samples of known moisture content. Materials varying in water content from a few to 100% can be analysed. The precision of the analysis is of the order of $\pm 0{\cdot}1\%$. In the other method, the width of the narrow central line from the moisture is measured. As the percentage of moisture present increases, the line width decreases and may become as narrow as 10^{-2} gauss. An empirical calibration curve is constructed as before. Although the latter method is limited to relatively low moisture contents (it becomes too insensitive at high moisture levels) it has the advantage that variations in the packing of the test sample are less critical.

Other analytical applications of wide-line n.m.r., of a similar nature to that described in the preceding paragraph, are the determination of the liquid content of fats[62] and the determination of the liquid content of liquid-solid slurries.[5]

The wide-line technique can be applied directly to solids. Because the possibilities of movement in solid systems are more restricted, the shape of the resonance absorption obtained from many solids is characteristic of the arrangement of the nuclei in the lattice. A study of the broad-line proton magnetic resonance spectrum of crystalline potassium trisoxalatorhodium hydrate obtained at a number of temperatures[63] has indicated that some of the protons in the crystal are present other than as water of crystallisation, and that the water of crystallisation can be grouped into at least three sets, the water molecules in different sets having different degrees of mobility. Wide-line n.m.r. has also been used for determining the degree of crystallinity of polymers[64] and, from observation of the changes in line width and shape with changes in temperature, for investigating order-disorder transitions in polymers.[65] A good example of such an application is seen in Fig. 2, which shows two superimposed lines, one narrow and one broad, presumed to be associated with the ^{19}F nuclei in the amorphous and crystalline regions, respectively, of polytetrafluorethylene (Teflon). With rising temperature the motional effects in the amorphous regions are more pronounced and more rapid, so that this signal narrows first. The broad component narrows abruptly at 293°K (not shown) and this abrupt narrowing appears to be associated with the first-order thermodynamic-transition point in Teflon.

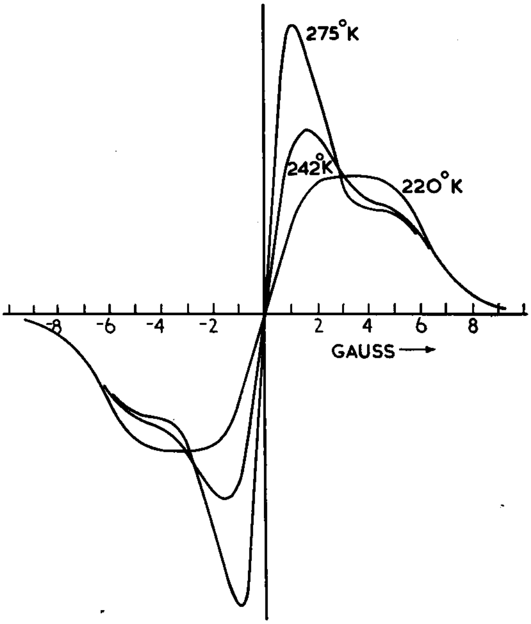

FIG. 2.—Absorption derivatives for the ^{19}F resonance in Teflon at 30 Mc/sec and the indicated temperatures (Wilson and Pake[64]).

Examples of the determination of hydrogen in solids by wide-line n.m.r. are the analysis of cerium hydride and zirconium hydroxide compounds by comparing the peak area of the signals with those obtained from standards.[59] An example of a direct fluorine determination on a solid is the analysis of fluorspar which contains more or less of one fluorine-containing species, calcium fluoride.[60] This sample was analysed by comparing the peak-to-peak amplitude of the signal with the linear calibration plot obtained for a series of fluorspar ores in which the fluorine content ranged from 34 to 46% fluorine by weight.

III. ELECTRON SPIN RESONANCE (ELECTRON PARAMAGNETIC RESONANCE)

(*A*) *Principles*

Whereas nuclear magnetic resonance utilises the energy levels of nuclei, electron spin resonance (e.s.r.) utilises those of electrons. The e.s.r. method is restricted, however, to systems possessing electrons whose spins are not paired, and whose magnetic moments are, therefore, not cancelled. The quantisation of the spatial orientation of the electron spins with respect to a static magnetic field results in discrete energy levels, just as with atomic nuclei possessing magnetic moments. Magnetic dipolar transitions may be induced between these energy levels by an alternating rf field whose frequency fulfills the resonance condition:

$$h\nu_0 = g\beta H_0 \tag{14}$$

where β is the Bohr magneton and g is the Landé or spectroscopic splitting factor, commonly referred to as the g value. For a static magnetic field of a few kilogauss the frequency of the radiation needed to include electron resonance lies in the microwave region of the spectrum.

The g value determines the position of the centre of the resonance, and has a value of 2·0023 for a completely free spin. Deviations from this value occur if there is an appreciable electronic orbital magnetic moment, and resonance will then occur either at higher or lower fields than that required for the free electron. To a good first approximation, orbital motion is completely quenched in nearly all organic free radicals, leaving the g values very close to that of a free spin. In transition metal compounds, however, the orbital contribution to the magnetic moment is often high, and g values differing widely from 2·0023 are found.

An e.s.r. spectrum may exhibit both fine and hyperfine structure. Where an atom or molecule has two unpaired electrons which interact strongly, a splitting of the electronic levels may result in fine structure being observed in the magnetic resonance spectrum. Apart from the case of biradicals no electronic splitting is possible in free radical spectra, but it is an important parameter in the e.s.r. study of many transition-metal ions. The hyperfine structure in a resonance spectrum arises from the interaction between the electron spin and the nuclear moments. This field may come from the nucleus of a paramagnetic ion itself or, in the case of a free radical, from a nucleus which is embraced in the molecular orbit of the electron. Because a nucleus of spin I may set itself in any of $2I + 1$ orientations, the vector sum of the external field and the nuclear field will have $2I + 1$ possible values, and the e.s.r. absorption line will be split into $2I + 1$ components. The splitting between the lines is termed a hyperfine splitting. This example illustrates hyperfine interaction in its simplest form. When more than one atomic nucleus in a given molecule can affect the resonance absorption, the final spectrum may be complicated. Fig. 3 shows the e.s.r. response of naphthacene positive ion, formed by dissolving naphthacene in concentrated sulphuric acid.[66] This molecule has three different kinds of proton positions with four protons in each class, and a spectrum of 125 lines might, therefore, be expected. One of the splittings, however, is within 1% of being three times another, and this results in 85 lines, 81 of which could be counted in the original spectrum. Although the detailed interpretation of an e.s.r. spectrum is not always possible, it is the occurrence and analysis of the hyperfine splitting which frequently makes high-resolution e.s.r. such an important tool for analytical purposes.

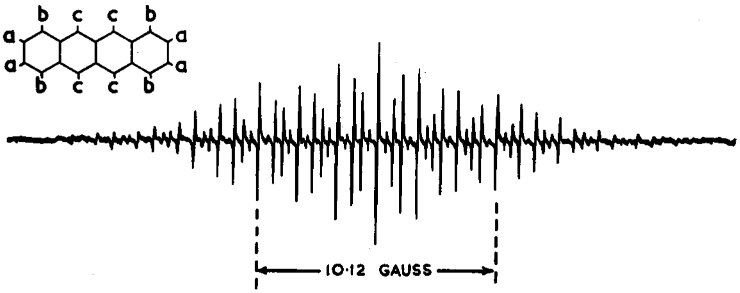

FIG. 3.—Hyperfine pattern (derivative tracing) of naphthacene positive ion (Hyde and Brown[66]).

Whilst in high-resolution n.m.r. the line widths are primarily determined by instrumental effects, in particular the homogeneity and stability of the magnetic field, the widths of the hyperfine components in an e.s.r. spectrum are governed by physical events within the sample itself, *i.e.*, by the relaxation phenomena. Three mechanisms by which relaxation occurs are: (1) spin–lattice interaction, (2) spin–spin interaction, (3) exchange interaction. Exchange interaction occurs when electrons are exchanged between the orbitals of different atoms or molecules. The effect is usually to average out the internal magnetic fields acting on the electrons, and thus narrow the line width. Exchange narrowing occurs only at high concentrations. The line widths observed in e.s.r. spectra vary from as little as 17 mgauss for free radicals in solution[67] to as much as 800 gauss for a paramagnetic ion in the solid state, even at 12°K.[68]

(*B*) *Experimental method*

The apparatus commonly used in e.s.r. studies differs from that used in n.m.r. studies chiefly in that microwave components replace conventional radiofrequency equipment. Although the choice of microwave frequency for optimum sensitivity depends among other factors on the nature of the sample, the most generally used frequency band is that centred on 10,000 Mc/sec (X-band). To achieve a higher sensitivity and to improve the resolution of the e.s.r. method, an a.c. modulation of the steady magnetic field, followed by phase-sensitive detection, is normally used in conjunction with a pen recorder to display the signal. The absorption line appears on the recorder as its first derivative, with respect to time. E.s.r. spectrometers which use a.c. modulation and phase-sensitive detection can now be obtained commercially.

For an introduction to the experimental techniques of e.s.r. the reader is referred to the literature (see *Bibliography*). Two recent advances in measurement technique will be mentioned here. A method by which an important gain in signal-to-noise ratio may be obtained has been described by Piette.[69] The output from an e.s.r. spectrometer is applied to a computer of average transients (CAT) with the result that the resonance signal is reinforced, because all additions of a positive signal are in phase. Noise signals, being random, are not in phase and thus average out. A signal-to-noise improvement factor of $\sqrt{n}$ is obtained where n is the number of times the spectrum is run. It should be noted that this technique is equally applicable to n.m.r., where it may be of special value when only small quantities of sample material are available.

With the methods commonly used for quantitative analysis by e.s.r., the unknown samples are compared with standards containing known concentrations of paramagnetic molecules, by measuring them successively and independently. The main experimental difficulty encountered is that different samples may perturb the measuring system in different ways. Thus, the intensity of absorption of a paramagnetic species depends, among other things, on the strength of the microwave magnetic field. Therefore, if the number of unpaired spins is to be determined, the strength of the microwave field must be kept rigidly constant when the comparisons of standards and unknowns are made. A recent device for comparative measurements of concentrations which avoids this and other sources of error is the double cavity.[70] In the double cavity two different samples can be placed at different maxima of the polarising magnetic field in the same microwave field. By arranging that the samples are in different polarising fields, overlap of their spectra is avoided. Using the double cavity it is possible to make exact determinations of the free-spin concentrations of samples with significant non-resonance absorption, especially of those containing water.

(*C*) *Applications of e.s.r.*

Because e.s.r. spectroscopy is only applicable to systems containing unpaired electrons its analytical capabilities are strictly limited, and the method will never rival n.m.r. in its importance to the analyst. Within its range, however, it is unexcelled both for sensitivity and speed. It is still a relatively young technique, which has undergone much slower instrumental development than that which has taken place with n.m.r. The full potential of e.s.r. as an analytical tool has certainly not been reached nor can it be truly evaluated at this early date.

Ingram,[71] Feher[72] and Fraenkel[73] have discussed in detail the factors that affect the sensitivity of the e.s.r. method. The theoretical limit of sensitivity approaches 10^9 unpaired spins. Realisable sensitivities at room temperature, with currently available commercial instruments, approach 10^{11} spins, or less than 10^{-12} mole, for an absorption line width of $\sim$2 gauss. This sensitivity is beyond that of other physical and chemical methods of quantitative analysis, and it can be improved by cooling the sample to low temperatures; severe cooling may, however, destroy the typical characteristics of the system under investigation. The highest sensitivities may be achieved only with samples of low dielectric loss. When aqueous or other samples showing high dielectric loss are used, it is necessary to use smaller volumes, *e.g.*, specimen tubes of 1 mm diameter instead of the more usual 5–6 mm diameter, to avoid excessive damping of the cavity and consequent reduction of sensitivity. Optimum e.s.r. signals with aqueous samples may be obtained by the use of flat quartz cells suitably oriented at the node of the electric field in the cavity.

Although the sensitivity of the e.s.r. method is high, the accuracy of quantitative measurements is often low. The inaccuracy arises, at least in part, because the recorded spectrum is usually a derivative trace and this must be integrated twice to obtain the signal intensity, and then compared with some standard, similarly treated. In these determinations of concentration the error may reach ±20%. If the line shape remains unchanged in a series of measurements and only relative concentrations of unpaired spins are required, integration may be dispensed with and measurements of peak-to-peak height on the derivative presentation used for comparison purposes. The error in such determinations of concentration should not exceed ±5% in favourable cases.

The analytical applications of e.s.r. will be surveyed here under three headings.

(*i*) *Free radicals.* A considerable amount of work utilising the e.s.r. technique simply as a method of detecting free radicals has been reported (*e.g.*, see references 74–78). Because the widths of the absorption lines observed for free radicals are usually quite small, strong signals are observed from small amounts. Radiation damage, however caused, commonly involves the rupture of bonds and the formation of free radicals, which may remain trapped in a solid structure. Many reports on e.s.r. studies in this field will be found in a collection of papers from a symposium on free radicals in biological systems.[79]

The e.s.r. technique has been used in many cases not only to detect, but also to identify free radicals. Analysis of the hyperfine structure of the resonance spectrum can be particularly useful in this respect.[71,80] The presence of the perinaphthenyl radical in the pyrolysis products of petroleum hydrocarbons has been inferred from the hyperfine pattern of the observed e.s.r. spectrum.[81] With free radicals of biological importance the resolution of hyperfine structure frequently fails because of molecular complexity. Even in this case, however, some general features can often be recognised, and identified with the same spectrum in simpler compounds.[82]

Although not nearly as useful as the hyperfine splitting for distinguishing radical spectra, the g value can be used for the purpose of identification. If the hyperfine structure is poorly resolved, it may, in fact, be the only determinable quantity which can be used to identify the radical. Because the g values of nearly all free radicals are within 0·5% of the free-spin value, precision measurements are required. An extensive study of the g values of semiquinone free radicals and hydrocarbon ions has been made.[83] The g values of a particular homologous series were found to vary in an apparently systematic manner. Observed shifts caused by changes in temperature, solvent and radical concentration were small compared to shifts caused by changes in molecular structure. An investigation of the nature of free radicals in petroleum asphaltenes has shown that the g values differ from those of the semiquinoid system, but are close to those of aromatic systems.[84] Peroxy radicals, $RO_2\cdot$, have no hyperfine structure detectable by present methods except that attributable to ^{17}O. Because of the difficulty of ^{17}O labelling, a method of identification based on the ^{17}O hyperfine splittings of free radicals is not yet broadly applicable. It has recently been shown[85] that the g values of peroxy radicals may distinguish them from free radicals of the type $R\cdot$ or $RO\cdot$.

Because the total intensity of the spectral lines is directly proportional to the number of unpaired spins present, the e.s.r. spectrum serves not only for identification purposes but also gives a direct measure of the concentration of free radicals. An example of such an application is the measurement of free radical concentration in low-temperature carbons.[86] Other examples are the estimation of the number of free radicals trapped during polymerisation,[87] and the number of radiation-induced free radicals in alanine and some related amino acids.[88] Hydroperoxides are usually determined by iodometry, but this method does not determine different types of hydroperoxide separately from their mixture. Electron resonance has now been used as an analytical technique for the determination of hydroperoxides in a solution, and can estimate a particular type of hydroperoxide in a mixture of several different hydroperoxides.[89] The e.s.r. method is based on the reaction between 1,1-diphenyl-2-picrylhydrazyl and hydroperoxides.

The ability to obtain free radical concentrations directly from the e.s.r. spectra makes the technique particularly useful for measuring the concentration of radical intermediates as a function of time. Free radicals which disappear at a slow rate are easily measured by merely following the decay of the e.s.r. signal with time. On the other hand, radicals with short lifetimes may be stabilised by freezing them at liquid nitrogen or liquid helium temperatures, and the actual concentration thus caught at any desired time interval. In this way rate constants of different chemical reactions and polymerisation processes have been determined (*e.g.*, see ref. 90). The e.s.r. spectrometer can also be used to study short-lived radical intermediates in chemical reactions under steady-state conditions by means of a flowing-sample technique.[91] The reactants are vigorously mixed at the entrance of the sample cell, and by varying the flow rate radicals can be observed within mseconds after mixing. A paper by Yamazaki, Mason and Piette[92] describes a typical kinetic application of the e.s.r. spectrometer to rapid free-radical reactions. Using a flow system, these workers were able to detect and identify free radicals from substrates, and to follow the kinetics of their formation and their subsequent decay during the oxidation of ascorbic acid and hydroquinone by peroxidase-hydrogen peroxide solutions.

It has been established that some aromatic hydrocarbons are oxidised to the corresponding cations at the surface of well-dried silica-alumina, and that the resulting species are stable in the adsorbed state.[93] These results have led to the development of an analytical method for the estimation of certain polynuclear hydrocarbons by e.s.r..[94] The e.s.r. method can detect less than 10^{-10} mole of hydrocarbon and its accuracy compares favourably with other spectroscopic methods of analysis at low concentrations. The resonance method depends for its success on the quantitative nature of radical formation on the catalyst surface. For each of the hydrocarbons studied (anthracene, perylene, dimethylanthracene and naphthacene) conversion into the radical form was found to be complete, within the limit of experimental error, over a wide range of concentration. The radical concentration in an unknown solution is determined by direct comparison of the signal amplitude (peak-to-peak height on the first derivative curve) for the unknown with that for a standard solution of the same radical. Using two such standards, the time required for a complete determination on a solution of unknown concentration is about 30 min. The method is accurate to about 5%.

(*ii*) *Transition-element ions.* The transition group elements are characterised by having unpaired electrons in the *d* and *f* orbitals, and their e.s.r. spectra usually differ from that given by free radicals. The *g* values of most free radicals remain close to the free-spin value of 2·0023 because there is very little coupling between the spin motion and any orbital motion. With paramagnetic atoms or ions the *g* value may vary over a wide range from 1 to 6 or more. This is because the electron is still bound to the paramagnetic atom, and thus has some interaction with the orbital motion *via* the spin-orbit coupling. In such cases the *g*-value variation can be very useful for distinguishing different spectra. Where the spin-orbit coupling is appreciable, the contribution from the orbital angular momentum is dependent on the relative orientation of the external magnetic field with respect to the paramagnetic ion and the resultant splitting of the energy levels is, therefore, anisotropic. In such cases a resolved spectrum can usually be obtained only by studying single crystals; in powders or solutions the anisotropic splitting gives rise to broad lines. If the ion has strong spin-lattice interaction, it will also be necessary to cool the specimen until the line width produced by this effect is less than that of the spin–spin interaction. With most of the ions in the rare-earth group, liquid helium temperatures are required to reduce the spin lattice interaction sufficiently for fine structure to be observed. The requirements for the iron group are less severe but, for many of the members, liquid hydrogen temperatures are necessary. Spin–spin interaction can be reduced by diluting with an isomorphous diamagnetic salt.

Typical spectra of transition-element ions extend over several hundreds of gauss and rarely contain resolved components as narrow as a few gauss. Fig. 4 shows the hyperfine structure of the e.s.r. spectrum of $^{55}Mn^{2+}$ (which possesses an isotropic g value) in water at room temperature. Other ions with isotropic g values include tervalent iron and tervalent gadolinium. The Mn^{2+} spectrum extends over $\sim$700 gauss. The six-line pattern results from the six $(2I + 1)$ possible magnetic orientations of the ^{55}Mn nucleus ($I = 5/2$) with respect to the applied magnetic field. Such a spectrum may be used to identify the Mn^{2+} ion, and its concentration may be estimated from comparative peak height measurements using a suitable standard. The method is a sensitive one. Spectra with a 10:1 signal-to-noise ratio may be obtained from aqueous solutions of 10^{-6} molarity using a flat quartz cell.[95] The technique has been used to detect trace paramagnetic elements, such as manganese or copper, as they occur in natural tissue,[96] and to investigate the concentration of manganese in certain micro-organisms.[97]

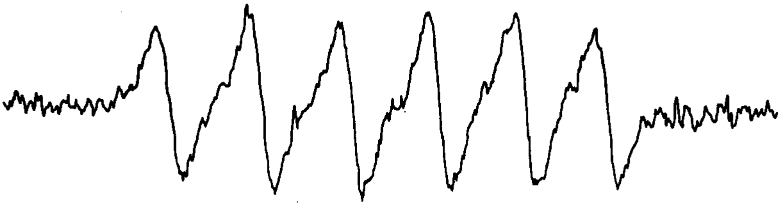

FIG. 4.—E.s.r. spectrum (first derivative) obtained from a $10^{-6}M$ aqueous solution of manganous ion (Varian Associates[95]).

The conversion of normally diamagnetic impurities into paramagnetic ones by excitation or by the attachment or removal of an electron has opened up another field of qualitative analysis. Various sources of irradiation may be used to bring about the conversion. For example, if quartz containing aluminium impurity is X-irradiated, the e.s.r. spectrum consists of six groups of lines each with six hyperfine lines.[98] This hyperfine structure may be accounted for by the unpaired electron being close to the aluminium impurity ion, which has a nuclear spin quantum number of 5/2.

Electron resonance has been used for the estimation of vanadium ion in petroleum distillates and residues.[99] In these investigations the most intense line of the vanadium absorption spectrum (first derivative curve) was used for quantitative analysis by directly comparing its height with that of a standard. Vanadium was detected down to at least 0·1 ppm, which makes e.s.r. spectroscopy applicable to vanadium analysis in practically all distillates. The time required for an estimation is only a few minutes.

(*iii*) *Atoms.* One of the intrinsic properties of atoms, with the exception of the rare gases, is that they all possess one or more unpaired electrons. Application of the e.s.r. technique to the gaseous phase is a recent development and it is likely that its use will be extended in the near future. Methods for using both diffusion and flow systems for detecting and estimating atoms in the gaseous phase have been described.[100]

The e.s.r. technique has been used to study the effect of water vapour on the dissociation of hydrogen in an electrical discharge.[101] The yield of hydrogen atoms was determined from the integrated intensity of the hydrogen hyperfine doublet. Both relative and absolute concentrations of oxygen atoms have been determined by e.s.r. spectroscopy in a study of the recombination process.[100] The maximum of the derivative of the absorption was used for making relative concentration measurements. Absolute concentrations were determined by comparing the atomic oxygen absorption with absorption by a known concentration of oxygen molecules, integrated intensities being employed for the comparison. The general theory relating the measured integrated intensities of e.s.r. absorption lines to the concentrations of odd-electron species in the gas phase has recently been reviewed and discussed in some detail by Westenberg and de Haas.[102] These authors then applied the theory in the form required for determining the absolute concentrations of oxygen, nitrogen and hydrogen atoms using molecular oxygen as the calibration gas. The determination of absolute oxygen and nitrogen atom concentrations by e.s.r. was shown to be a reliable experimental technique by comparison with the independent results of titration with nitrogen dioxide and nitric oxide, respectively.

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Résumé—On décrit brièvement les principes des résonances magnétiques nucléaire et électronique, en relation avec l'emploi de ces techniques en chimie analytique. On passe en revue un large champ d'applications analytiques afin de mettre en évidence le domaine et les limitations de ces méthodes.

Zusammenfassung—Die Grundlagen der magnetischen Kern- und Elektronenresonanz werden unter Berücksichtigung ihres Gebrauchs in der analytischen Chemie kurz beschrieben. Es wird eine Übersicht über ein breites Spektrum analytischer Anwendungen gegeben, um den Einsatzbereich dieser Methoden und dessen Grenzen zu zeigen.

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SHORT COMMUNICATIONS

A thermogravimetric pyrolysis study of the interaction of di(1,2,3-benzotriazolatium)hexacyanoruthenate(IV) with certain organic amines

(*Received* 26 *November* 1964. *Accepted* 22 *December* 1964)

This paper arises from a study of the products obtained through the interaction of di(1,2,3-benzotriazolatium)hexacyanoruthenate(IV) with certain organic amines.[1] In earlier papers information was presented on the interaction of certain organic amines with 1,2,3-benzotriazole derivatives of cyano complexes of the platinum group elements.[2,3] Pyrolytic results obtained for the amine derivatives gave support to the proposed formulae of the products formed in the interaction of di(1,2,3-benzotriazolatium)hexacyanoruthenate(IV).

EXPERIMENTAL

Apparatus and material

The thermobalance and its calibration, operation, and use have been reported previously.[4] The temperature of the combustion chamber was increased at an average of 3°/min over a temperature interval from room temperature to 750°. A Beckman IR-5-Spectrophotometer was used for obtaining infrared spectra of various decomposition products, using a standard potassium bromide-pellet technique and sodium chloride cells.

All precipitates were prepared according to the procedure of Wilson and Merchant.[1] The precipitates were filtered using fine-porosity, sintered-glass crucibles. The compounds were dried for 10 hr in a vacuum desiccator, using magnesium perchlorate as the desiccant.

RESULTS

Pyrolysis curves of the compounds with respective formulae:

(1) $(C_2H_5NH_3)_2Ru(CN)_6$; (2) $(C_6H_5NH_3)_2(C_6H_5NH_2)_2Ru(CN)_6$;
(3) $(CH_3NH_3)_2(CH_3NH_2)_2Ru(CN)_6$; (4) $[(C_2H_5)_2NH_2]_2[(C_2H_5)_2NH]_2Ru(CN)_6$;
(5) $[(CH_3)_2NH_2]_2[(CH_3)_2NH]_2Ru(CN)_6$; (6) $(p\text{-}C_6H_4NH_3NH_2)_2Ru(CN)_6$;
(7) $[CH(CHCH)_2NH]_2Ru(CN)_6$; (8) $(CH_3)_4N(C_6H_4N_2NH_2)Ru(CN)_6$;
(9) $(m\text{-}C_6H_4NH_3NH_2)_2Ru(CN)_6$

are presented graphically in Figs. 1–3 and the analysis of the curves is given in Table I. The plateau at C_2 which persists up to the 750° limit of this study corresponds to indefinite mixtures of ruthenium

TABLE I

	C_1			C_2	
Compounds	Initial weight, *mg*	Weight corrected for moisture, *mg*	Temp. range, °*C*	Weight of ruthenium residue obtained, *mg*	Temp. range, °*C*
1. $(C_2H_5NH_3)_2Ru(CN)_6$	21·1	20·0	<110	4·2	>257
2. $(C_6H_5NH_3)_2(C_6H_5NH_2)_2Ru(CN)_6$	22·3	21·7	<53	5·6	>337
3. $(CH_3NH_3)_2(CH_3NH_2)_2Ru(CN)_6$	26·2	25·8	<65	6·3	>466
4. $[(C_2H_5)_2NH_2]_2[(C_2H_5)_2NH]_2Ru(CN)_6$	19·9	19·8	<61	3·6	>586
5. $[(CH_3)_2NH_2]_2[(CH_3)_2NH]_2Ru(CN)_6$	24·4	24·0	<159	6·3	>532
6. $(p\text{-}C_6H_4NH_3NH_2)_2Ru(CN)_6$	26·5	26·1	<151	5·2	>641
7. $[CH(CHCH)_2NH]_2Ru(CN)_6$	25·1	25·1	<30	5·4	>210
8. $(CH_3)_4N(C_6H_4N_2NH_2)Ru(CN)_6$	26·2	25·9	<65	5·7	>391
9. $(m\text{-}C_6H_4NH_3NH_2)_2Ru(CN)_6$	26·7	26·4	<128	6·2	>607

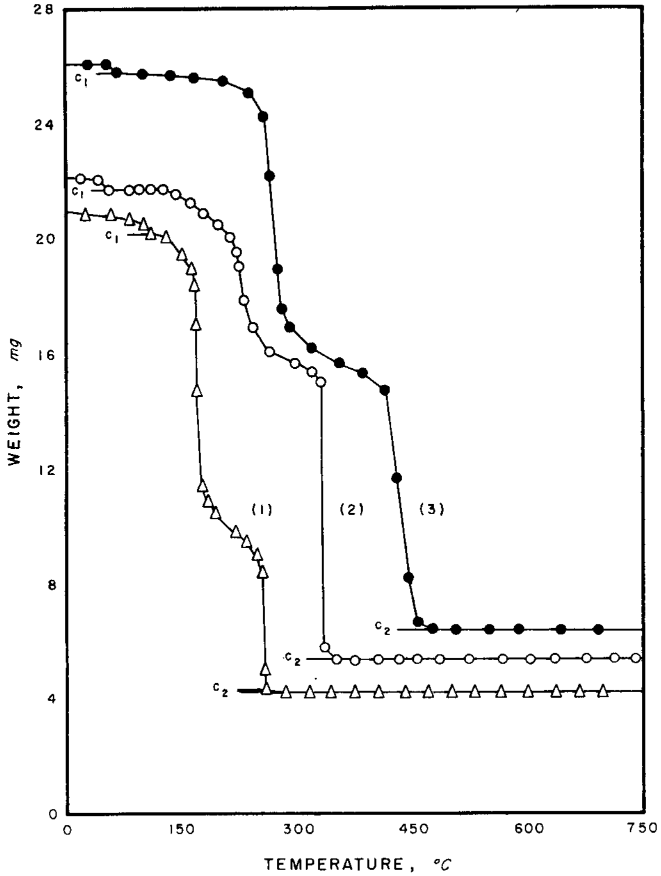

FIG. 1.—Thermogravimetric analysis of compounds 1-3:

1. $(C_2H_5NH_3)_2Ru(CN)_6$ —△—
2. $(C_6H_5NH_3)_2(C_6H_5NH_2)_2Ru(CN)_6$ —○—
3. $(CH_3NH_3)_2(CH_3NH_2)_2Ru(CN)_6$ —●—

and/or ruthenium oxides. The thermal decomposition of the amine derivatives is probably best explained by the following reactions:

1. $(C_2H_5NH_3)_2Ru(CN)_6$

$$\xrightarrow[\text{Air}]{110^\circ\text{–}257^\circ} \quad 2(C_2H_5)NH_2\uparrow + 2HCN\uparrow + 2(CN)_2\uparrow + \text{ruthenium residue}$$

2. $(C_6H_5NH_3)_2(C_6H_5NH_2)_2Ru(CN)_6$

$$\xrightarrow[\text{Air}]{53^\circ\text{–}337^\circ} \quad 4C_6H_5NH_2\uparrow + 2HCN\uparrow + 2(CN)_2\uparrow + \text{ruthenium residue}$$

3. $(CH_3NH_3)_2(CH_3NH_2)_2Ru(CN)_6$

$$\xrightarrow[\text{Air}]{65^\circ\text{–}466^\circ} \quad 4CH_3NH_2\uparrow + 2HCN\uparrow + 2(CN)_2\uparrow + \text{ruthenium residue}$$

4. $[(C_2H_5)_2NH_2]_2[(C_2H_5)_2NH]_2Ru(CN)_6$

$$\xrightarrow[\text{Air}]{61^\circ\text{–}586^\circ} \quad 4(C_2H_5)_2NH\uparrow + 2HCN\uparrow + 2(CN)_2\uparrow + \text{ruthenium residue}$$

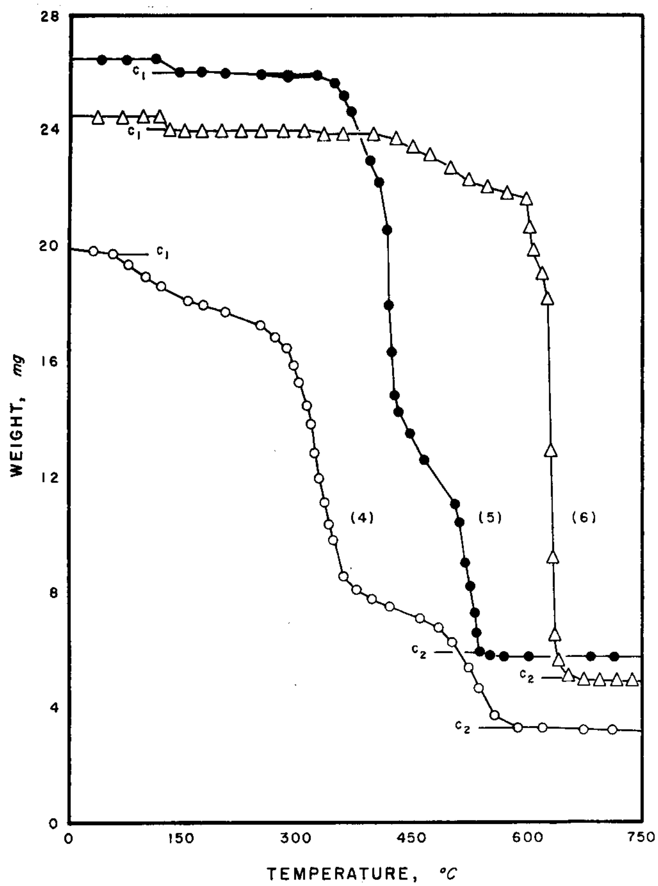

FIG. 2.—Thermogravimetric analysis of compounds 4-6:

4. $[(C_2H_5)_2NH_2]_2[(C_2H_5)_2NH]_2Ru(CN)_6$ —○—
5. $[(CH_3)_2NH_2]_2[(CH_3)_2NH]_2Ru(CN)_6$ —●—
6. $(p\text{-}C_6H_4NH_3NH_2)_2Ru(CN)_6$ —△—

5. $[(CH_3)_2NH_2]_2[(CH_3)_2NH]_2Ru(CN)_6$

$$\xrightarrow[\text{Air}]{159°\text{–}532°} 4(CH_3)_2NH\uparrow + 2HCN\uparrow + 2(CN)_2\uparrow + \text{ruthenium residue}$$

6. $(p\text{-}C_6H_4NH_3NH_2)_2Ru(CN)_6$

$$\xrightarrow[\text{Air}]{151°\text{–}641°} 2(p\text{-}C_6H_4NH_2NH_2)\uparrow + 2HCN\uparrow + 2(CN)_2\uparrow + \text{ruthenium residue}$$

7. $[CH(CHCH)_2NH]_2Ru(CN)_6$

$$\xrightarrow[\text{Air}]{30°\text{–}210°} 2CH(CHCH)_2N\uparrow + 2HCN\uparrow + 2(CN)_2\uparrow + \text{ruthenium residue}$$

8. $(CH_3)_4N(C_6H_4N_2NH_3)Ru(CN)_6$

$$\xrightarrow[\text{Air}]{65°\text{–}391°} (CH_3)_4NCN\uparrow + C_6H_4N_2NH\uparrow + HCN\uparrow + 2(CN)_2\uparrow + \text{ruthenium residue}$$

9. $(m\text{-}C_6H_4NH_3NH_2)_2Ru(CN)_6$

$$\xrightarrow[\text{Air}]{128°\text{–}607°} 2(m\text{-}C_6H_4NH_2NH_2)\uparrow + 2HCN\uparrow + 2(CN)_2\uparrow + \text{ruthenium residue}$$

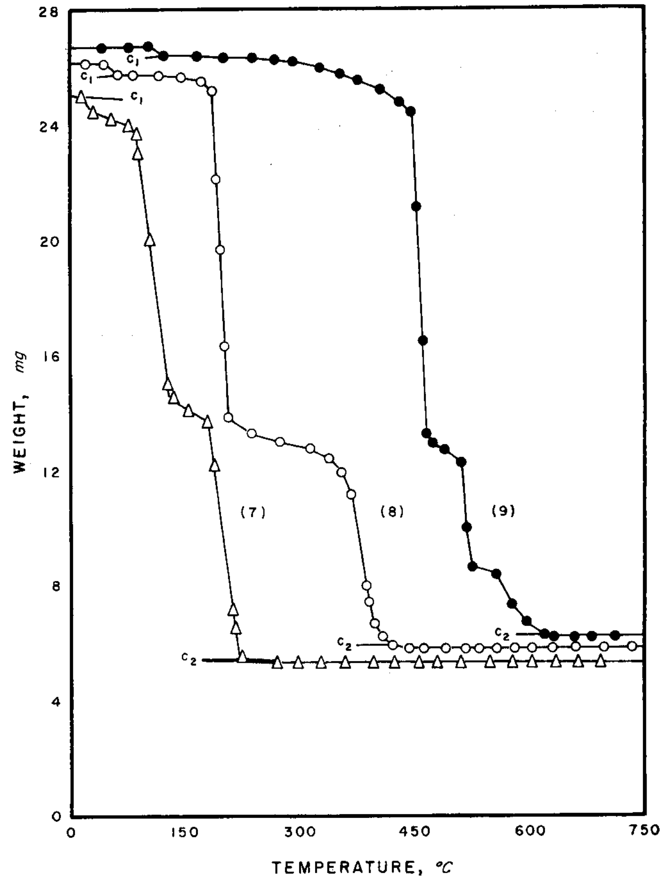

Fig. 3.—Thermogravimetric analysis of compounds 7-9:

7. $[CH(CHCH)_2NH]_2Ru(CN)_6$ —△—
8. $(CH_3)_4N(C_6H_4N_2NH_2)Ru(CN)_6$ —○—
9. $(m\text{-}C_6H_4NH_3NH_2)_2Ru(CN)_6$ —●—

Isolation of pyrolytic products

The pyrolysis results presented for the thermogravimetric determinations of the amine derivatives obtained through the interactions of di(1,2,3-benzotriazolatium)hexacyanoruthenate(IV) with certain organic amines suggest the presence of several decomposition products. To further verify the presence of certain decomposition products, 1-g samples of the respective amine derivatives were separately decomposed in a special decomposition apparatus as described by Wilson and James.[5] The coolant (CO_2) was sufficient to condense *m*-phenylenediamine and *p*-phenylenediamine from their respective amine derivatives, and 1,2,3-benzotriazole from the tetramethylammonium chloride derivative. The presence of aniline was verified by decomposing a 1-g sample of the amine derivative and allowing the resulting vapours to dissolve in water. On the addition of hydrogen chloride to the solution, aniline hydrochloride was obtained. The vapours resulting from the diethylamine, ethylamine, methylamine, dimethylamine and pyridine derivatives were each dissolved in separate carbon tetrachloride solutions. In all cases the infrared spectra obtained from the aniline hydrochloride and the respective amine samples contained all of the principal absorbance bands corresponding to the infrared spectra of the respective pure samples. The presence of hydrogen cyanide and/or cyanogen was verified by decomposing 1-g samples of the respective amine derivatives and allowing the vapours to dissolve in aqueous silver nitrate solution. In each case a white precipitate of silver cyanide was obtained.

DISCUSSION

In this study the thermobalance was employed to follow the pyrolysis reactions taking place in certain complex interaction products obtained through the interaction of several organic amines and tetramethylammonium chloride with di(1,2,3-benzotriazolatium)hexacyanoruthenate(IV). Decomposition of the amine derivatives gave hydrogen cyanide and/or cyanogen, the respective amine, a ruthenium residue and in one case 1,2,3-benzotriazole and tetramethylammonium cyanide.

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Summary—The thermogravimetric pyrolysis of the interaction products of certain organic amines and tetramethylammonium chloride with di(1,2,3-benzotriazolatium)hexacyanoruthenate(IV) is reported in this study.

Zusammenfassung—Es wird über die thermogravimetrische Pyrolyse der Reaktionsprodukte einiger organischer Amine und Tetramethylammoniumchlorid mit Di(1,2,3-benztriazolatium)hexacyanoruthenat (IV) berichtet.

Résumé—On décrit la pyrolyse thermogravimétrique des produits d'interaction de certaines amines organiques et du chlorure de tétraméthylammonium avec l'hexacyanoruthénate(IV) de di (1,2,3-benzotriazolatium).

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Coprecipitation of iron(III) and zinc ions with aluminium tris-(8-hydroxyquinolate)

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IN a previous paper[1] a study was presented of the coprecipitation of tracer quantities of radioactive scandium, yttrium, cerium(III) and indium with milligram quantities of aluminium precipitated as the tris-(8-hydroxyquinolate) by slow isothermal evaporation of aqueous acetone solutions. For these systems it was concluded that coprecipitation of the tracer (M) remained small over almost the complete range of precipitation of the carrier unless the tracer took the form $M(C_9H_6ON)_3$. This conclusion has now been examined in relation to the behaviour of iron(III) and zinc as tracers.

EXPERIMENTAL

The reagents, apparatus and procedure were those used in the earlier investigation with the following additions or modifications.

Tracers. Iron-59 (containing some inactive iron) and carrier-free zinc-65 were obtained (in 0·1*M* and 1*M* hydrochloric acid, respectively) from the Radiochemical Centre, Amersham, England. Dilute solutions of each isotope were prepared in 0·1*M* hydrochloric acid as required.

Counting. Counting was performed by means of a well-type sodium iodide (thallium activated) scintillation counter.

Procedure. In experiments 9, 10 and 11 of Table I, the final measurements were made on aliquots of solutions prepared by diluting the filtrates with acetone to the volumes they occupied before evaporation.

Infrared spectra. The infrared spectra were obtained from Nujol mulls in the 2·5 to 25 μ region using a Grubb-Parsons double-beam grating spectrophotometer.

RESULTS AND DISCUSSION

Milligram amounts of iron and zinc are precipitated quantitatively from acetic acid-acetate solution.[2] The former is obtained[2,3] as $Fe(C_9H_6ON)_3$ on drying at 120°, the latter as $Zn(C_9H_6ON)_2 . xH_2O$ where x is variable and depends on the drying temperature.[2,4] If the pattern of behaviour previously observed is followed, iron(III) would be expected to show similarities to indium, and zinc to the rare-earth ions.

The results recorded in Table I for the coprecipitation of tracer quantities of iron with aluminium tris-(8-hydroxyquinolate) are in agreement with the predicted behaviour. Values of D and λ show that the distribution of tracer follows the logarithmic law of Doerner and Hoskins.[5] The results may be compared with those obtained with indium as tracer when the fractional precipitation of tracer and carrier so nearly coincided over the whole range of precipitation that a distinction between the two limiting types of distribution could not be made. It has been reported[2] that iron(III) salts yield the tris-(8-hydroxyquinolate) from solutions containing as much as 25% acetic acid-sodium acetate. Acetate is, therefore, not expected to influence the tracer iron distribution appreciably; this conclusion finds support from the few measurements (Table I, experiments 12, 13, 14 and 15) made at lower acetate concentrations and from the observation that iron precipitated from aqueous acetone in the same molar quantity and under the same conditions as aluminium when used as carrier, gave the product $Fe(C_9H_6ON)_3$ on drying at 130°. The solubility of the iron compound, which is granular, appears to be quite low relative to that of aluminium in aqueous acetone.

TABLE I.—COPRECIPITATION OF IRON* WITH ALUMINIUM

No.	Al pptd., %	Fe copptd., %	D	λ
1	7·90	10·7	1·40	1·36
2	29·5	38·9	1·52	1·41
3	30·3	42·9	1·73	1·55
4	39·4	51·5	1·63	1·44
5	50·9	65·3	1·81	1·48
6	58·3	74·1	2·05	1·55
7	61·1	73·5	1·77	1·41
8	68·2	80·8	1·96	1·44
9	78·8	89·8	2·37	1·47
10	78·2	90·5	2·66	1·55
11	84·7	94·1	2·88	1·51
12	12·8	17·1	1·41	1·37
13	21·7	30·8	1·61	1·51
14	48·6	63·1	1·81	1·50
15	61·6	77·6	2·16	1·56

* About 1×10^{-8} mole of iron was present in the system during each precipitation. Using the general procedure outlined previously[1] 40 ml of 2·0*M* ammonium acetate were used in experiments 1–11 and 40 ml of 0·20*M* in the remainder.

TABLE II.—THE COPRECIPITATION OF ZINC-65 FROM SOLUTIONS TO WHICH WERE ADDED 40 ml OF 2·0*M* AMMONIUM ACETATE

Al pptd., %	21·49	31·98	40·15	48·95	61·52	81·40	83·45
Zn copptd., %	0·421	0·526	0·547	0·874	1·14	1·06	0·925
Al pptd., %	87·60	98·2	99·83	100	100		
Zn copptd., %	0·810	1·82	4·72	4·98	41·1		

See ref. 1 for other conditions.

The coprecipitation of zinc under the three sets of conditions employed is, in general, as predicted. The results may be compared with those obtained previously for tracer yttrium. In the presence of much acetate (Table II) coprecipitation of zinc does not change appreciably until aluminium has precipitated completely. It then shows (at least apparently) a variable degree of coprecipitation, which seems to depend on the time elapsing between complete precipitation and filtration, although other factors, such as the nature of the container surface may contribute. Neither D nor λ is constant and calculated values are not presented.

TABLE III.—COPRECIPITATION OF ZINC WITH ALUMINIUM IN DILUTE ACETATE SOLUTION AND IN THE ABSENCE OF ACETATE

No.	Al pptd., %	Zn copptd., %	$D \times 10^2$	$\lambda \times 10^2$
1	23·5	0·621	2·03	2·23
2	28·7	0·841	2·10	2·50
3	51·5	2·16	2·08	3·03
4	55·6	1·81	1·47	2·26
5	63·0	2·75	1·66	2·80
6	66·3	3·03	1·59	2·82
7	77·8	3·45	1·02	2·33
8	83·4	3·57	0·739	2·03
9	7·78	0·262	3·11	3·24
10	14·3	0·364	2·20	2·36
11	25·2	0·430	1·29	1·48
12	25·3	0·588	1·75	2·02
13	49·6	0·896	0·919	1·31
14	66·4	1·91	0·984	1·77
15	76·6	2·14	0·670	1·49
16	77·0	2·26	0·692	1·56
17	80·8	3·01	0·739	1·85
18	87·1	2·75	0·420	1·36

* Nos. 1–8 were carried out using 40 ml of 0·20*M* ammonium acetate and Nos. 9–18 had 15 ml of 0·100*M* sodium hydroxide + 25 ml of water replacing the ammonium acetate in the general procedure.[1]

In the absence of acetate (experiments 9–18, Table III) coprecipitation of zinc is a little higher and shows a steeper dependence on fractional precipitation of the carrier. However, although the precision of the zinc measurements is not as good as that for other systems studied, significantly higher values were obtained using more dilute acetate solutions than in the absence of this ion (Table III). Values of D and λ calculated for results obtained in the absence of acetate and in dilute acetate show that λ has a rough constancy for each series separately, but values of D decrease progressively with increasing fractional precipitation of the aluminium (Table III).

The explanation for the observed dependence of zinc coprecipitation on the medium is not clear. A thermogravimetric study of picolates and dipicolates of certain rare-earths[6] shows that solvates obtained directly on precipitation may depend on the pH of the medium from which precipitation occurs and it is possible that a similar dependence exists in the zinc coprecipitation. However, although conditions are not strictly comparable to those pertaining to the tracer experiments, when zinc replaces the same molar quantity of aluminium an identical product, as determined by its infrared spectrum, is isolated from solutions of the three compositions discussed. Some portions of the products examined were air dried at 130° and others for about 1 week at the laboratory temperature (20 ± 2°). Analysis of part of the precipitate obtained from the strong acetate medium and dried at 130° gave Zn, 18·4%; C, 61·1%; H, 3·43% [$Zn(C_9H_6ON)_2$ requires Zn, 18·5%; C, 61·1%; H, 3·42%]. The same precipitate dried at 20° gave Zn, 16·9%; C, 55·8%; H, 4·37%; H_2O, 9·01% [$Zn(C_9H_6ON)_2.2H_2O$ requires Zn, 16·8%; C, 55·5%; H, 4·14%; H_2O, 9·25%]. The precipitate, like that obtained previously with yttrium, has a low solubility relative to aluminium in aqueous acetone and is flocculent, suggesting extensive hydrogen bonding.

While structural differences are undoubtedly important in determining the extent of coprecipitation it is unlikely that dynamic factors can be ignored in discussing these results in detail. The rate of deposition of carrier on growing crystallite surfaces[7] will affect λ and in the experiments discussed is controlled by the rate of evaporation of the solvent, which in turn is influenced by the nature and concentrations of the solutes and the solvent composition. Clearly, much additional work is required to examine such possible contributing factors.

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S. J. LYLE®*

Summary—Coprecipitation of tracer quantities of iron(III) and zinc with aluminium precipitated as the 8-hydroxyquinolate by isothermal evaporation of aqueous acetone solutions has been examined radiochemically. Iron(III) coprecipitation follows the logarithic distribution law with $\lambda = 1{\cdot}47 \pm 0{\cdot}07$ for a wide range of acetate concentrations. Zinc shows similarities to yttrium and other rare-earth ions in only coprecipitating to a small extent, except on complete precipitation of the carrier. Results obtained from different media show small but distinguishable differences, particularly with increasing fractional precipitation of the carrier.

Résumé—On a étudié, par radiochimie, la coprécipitation du fer (III) et du zinc, en très petites quantités, à l'état de traceurs, avec l'aluminium, précipité à l'étet de 8-hydroxyquinoléinate, par évaporation isotherme de la solution hydroacétonique. La coprécipitation du fer (III) suit la loi de répartition logarithmique, avec $\lambda = 1{,}47 \pm 0{,}07$, dans un large domaine de concentrations en acétate. Le zinc présente des analogies avec l'yttrium et d'autres ions de terres rares, par le fait qu'il ne coprécipite que pour une faible partie, sauf en cas de précipitation totale de l'entraîneur. Les résultats obtenus à partir de différents milieux ont montré des différences petites mais nettes, en particulier lors de la précipitation fractionnée croissante de l'entraîneur.

Zusammenfassung—Die Mitfällung von Tracermengen Eisen (III) und Zink mit Aluminium, das als 8-Hydroxychinolinat durch Eindunsten der wäßrig-acetonischen Lösung gefällt wird, wurde radiochemisch untersucht. Die Mitfällung von Eisen (III) folgt dem logarithmischen Verteilungsgesetz mit $\lambda = 1{,}47 \pm 0{,}07$ in einem weiten Bereich der Acetatkonzentration. Zink ähnelt Yttrium und anderen seltenen Erden; es wird nur wenig mitgefällt, außer bei völliger Ausfällung des Trägers. Die Ergebnisse aus verschiedenen Medien zeigen kleine, aber merkliche Unterschiede, besonders bei Ansteigen des ausgefällten Trägeranteils.

REFERENCES

[1] S. J. Lyle and D. L. Southern, *Talanta*, 1964, **11**, 1239.
[2] F. J. Welcher, *Organic Analytical Reagents*, Vol. I. D. van Nostrand Co. Inc., New York, 1947, Chapter XIII.
[3] C. Duval and Dat Xuong, *Analyt. Chim. Acta*, 1951, **5**, 160.
[4] M. de Clerq and C. Duval, *ibid.*, 1951, **5**, 282.
[5] H. Doerner and W. Hoskins, *J. Amer. Chem. Soc.*, 1925, **47**, 662.
[6] L. Moyne and G. Thomas, *Analyt. Chim. Acta*, 1963, **29**, 66.
[7] D. H. Klein and B. Fontal, *Talanta*, 1965, **12**, 35.

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* Present address: The Chemical Laboratory, University of Kent, Canterbury, England.

Talanta, 1965, Vol. 12, p. 567. Pergamon Press Ltd. Printed in Northern Ireland

LETTER TO THE EDITOR

Interlingua

SENIOR,

ESSEVA facilissimo de leger quel littera de Dr. Rieman[1] e credo que le majoria del chemistas pote leger alsi iste littera scribite sensa dictionarios o grammaticas de interlingua. Ora non esiste un metodo por scribire sistematicamente le chimicas in iste lingua ma non esserea multo difficile de far lo. Io provava cum nulla instructione in interlingua de traducer in "pidgin-interlingua" le articulos anglese in le littera de Professor Wilson: "... un novo analitico metodo esse introdotto pro (le analisso de) moleculi fluorescenti—analisso estingue—fluorescentia. Iste campo de ricerca avera applicationi grandi in analisso organico por traccias. Uso analitico esse fatto del effetto de estinguere in spectrofoto-fluorometria. Sostantias come antracene, fenantrene pyrene, benz(a)antracene, benzo(a)pyrene, perylene etc. esse stati trovati a esser non-fluorescenti in solutione de nitrometane, ma idrocarbonas contenenti il cercolo fluorantene esse fluorescenti".

However, I do not see how Interlingua, which is obviously based on Latin roots, could be any more understandable to readers (*e.g.*, Slavs or Orientals) knowing no Romance language than naturally existing members of this language group such as French, Italian and Spanish.

I feel, sir, that it would be far more useful for *Talanta* to publish papers in English, French, German or Russian and to give longer, more detailed abstracts in whichever three of these languages was not used by the author.

J. HALL

Morganite Research and Development Ltd.
Battersea Church Road
London S.W. 11, *England.*
22 *February* 1965

REFERENCE

[1] Wm. Rieman III, *Talanta*, 1965, **12**, 192.

Talanta, 1965, Vol. 12, pp. i to iii. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

CANADA

Monday–Wednesday 18–20 *October* 1965: **Twelfth Ottawa Symposium on Applied Spectroscopy:** *Canadian Association for Applied Spectroscopy.* Ottawa.

Papers are invited dealing with all fields of spectroscopy; investigations in which novel applications of spectroscopy were used; and applications of other techniques to problems in spectroscopy, such as electronic computers and high-speed photography.

Titles and brief abstracts of papers should be submitted as soon as possible to Mr. R. V. Baker, Aluminium Company of Canada Ltd., Arvida, Ottawa; the final date for acceptance of papers is June 15.

DEUTSCHE DEMOKRATISCHE REPUBLIK

28.9.–2.10. 1965: **2. International Symposium Reinststoffe in Wissenschaft und Technik:** *Chemische Gesellschaft in der DDR, Gesellschaft Deutscher Bergund Hüttenleute* und *Physikalische Gesellschaft in der DDR.* Dresden.

Sektion C: Reinststoff-Analytik

Bestimmung chemischer Verunreinigungen mit modernen physikalischen und chemischen Verfahren—Spezielle Berücksichtigung methodischer Weiterentwicklungen

Sektion D: Realstruktur

Nachweis von Kristallbaufehlern mittels Röntgen-, Elektroden- und Neutronenstrahlen sowie mit metallographischen Methoden—Entstehung, Verhalten und Eigenschaften von Gitterstörungen

Sitz des Organisationskomitees: Chemische Gesellschaft in der DDR, Berlin W8, Clara-Zetkin-Str. 105.

FRANCE

Mercredi 2-6-1965: Réunion commune avec la Section de Chimie Analytique de la Société de Chimie Industrielle.

Mecredi 2-6-1965: L'analyse fonctionnelle au service de la synthèse organique, par M. F. Pellerin, à 17 h 45, à la Faculté de Pharmacie de Paris.

GREECE

Sunday–Friday 19–24 *September* 1965: **Methods of Immediate Separation and Chromatography:** *Association of Greek Chemists* in collaboration with *Association for Development of Spectrographic Methods* (*G.A.M.S.*). Athens.

The principal subject will be Chromatography in the general sense, its theoretical aspects, apparatus and analytical applications. The following plenary lectures will be presented:

Some recent progress in chromatography.	E. Lederer
Identification of gas chromatographic fractions.	D. Ambrose
A comparison of thin layer and paper chromatography.	F. H. Pollard

Further information can be obtained from Professor G. Parissakis, Association of Greek Chemists, 27 Kaningos Road, Athens, Greece.

ÖSTERREICH

"**Symposium analytische Chemie**", Treffen jugoslawischer, ungarischer und österreichischer Chemiker. (Im Anschluß an die Hauptversammlung des Vereines Österreichischer Chemiker.)

Graz, 29. *September* bis 1. *Oktober* 1965.

Hauptvortrage: B. Kosta (Jugoslawien), E. Pungor (Ungarn), V. Gutmann (Wein).

Kolloquium für metallkundliche Analyse und Elektronenstrahlmikroanalyse, veranstaltet vom Institut für analytische Chemie und Mikrochemie der Technischen Hochschule in Wien und der Österreichischen Gesellschaft für Mikrochemie und Analytische Chemie.

Wein, 20. bis 23, *Oktober* 1965, *Technische Hochschule in Wien.*

UNITED KINGDOM

Monday–Thursday 6–9 *September* 1965: **First International Conference on Thermal Analysis.** Department of Natural Philosophy, University of Aberdeen, Old Aberdeen, Scotland.

As indicated previously [*Talanta*, 1965, **12** (1), ii], the theme will be

Thermal Techniques and Their Applicability

and the conference will have the following Sections:

1. Advances in instrumentation.
2. Organic materials, including polymers.
3. Inorganic materials and metallurgy.
4. Physical chemistry and quantitative aspects.
5. Minerals.
6. Applied sciences (building materials, ceramics, *etc.*).

The number of papers that has been offered is such that it will be necessary to hold two sessions of most, if not all, Sections. In consequence, it will be impossible to avoid simultaneous meetings, but in arranging such sessions attention will be paid to the numbers interested in each of the Sections.

Each session of each Section will be presided over by a prominent worker in the field and, at the invitation of the Organising Committee, Dr. J. P. REDFERN, Dr. C. B. MURPHY, Professor Dr. L. G. BERG and Professor Dr. R. BARTA will deliver opening lectures at the first sessions of Sections 1, 2, 3 and 6, respectively.

If not already paid, the registration fee of £5 sterling ($15.00 U.S. or 13 roubles) is now due and must be paid by 15 May, 1965. Further information may be obtained from Dr. R. C. MACKENZIE, Macaulay Institute for Soil Research, Craigiebuckler, Aberdeen, Scotland.

Wednesday–Friday 13–15 *October* 1965: **1965 Symposium on Automated Analytical Chemistry:** Technicon Instruments Company Ltd. London.

As in previous years, the Symposium will be on an International basis and original work by distinguished scientists from Europe and America will be presented, as well as contributions from workers in United Kingdom.

The *Society for Analytical Chemistry* has approved the formation of a *Thermal Analysis Group*, which will be concerned with methods of investigation normally performed under dynamic conditions of temperature.

The Officers of the first Committee of the new Group are:

Chairman: R. C. MACKENZIE
Vice-Chairman: J. P. REDFERN
Hon. Secretary: C. J. KEATTCH
Hon. Treasurer: A. A. HODGSON

Members of the Society for Analytical Chemistry may become members of the Group on request to the Secretary of the Society, 14 Belgrave Square, London S.W.1. Those who are not members of the Society may receive notices of the meetings of the Group on application to its Secretary, Mr. C. J. KEATTCH, John Laing Research and Development Ltd., Manor Way, Boreham Wood, Herts.

British Standards Institution has announced the following *Revised British Standard:*

B.S. 2690: *Methods of testing water used in industry: Part* 2: 1965: *Dissolved oxygen, hydrazine and sulphite.* This gives three methods for dissolved oxygen, one method for hydrazine and one method for sulphite. (*Price* 7s.6d.)

The following *Amendment Slip* is also announced:

B.S. 3762: 1964: *Methods of sampling and testing detergents. Amendment No.* 1: *PD* 5446. (*Gratis.*)

UNITED STATES OF AMERICA

Monday–Friday 7–11 *June* 1965: **International Carbon-14 and Tritium Dating Conference.** Washington State University, Pullman, Wash.

Wednesday–Friday 9–11 *June* 1965: **Summer Symposium on Bioanalytical Techniques:** *Division of Analytical Chemistry of American Chemical Society* and ANALYTICAL CHEMISTRY. University of Wisconsin, Madison, Wis.

Sunday–Friday 13–18 *June* 1965: **Sixty-Eighth Annual Meeting:** *American Society for Testing and Materials.* Purdue University, Lafayette, Ind.

Monday–Thursday 14–17 *June* 1965: **Sixteenth Mid-America Symposium on Spectroscopy.** Sheraton-Chicago Hotel, Chicago, Ill.

Monday–Tuesday 14–15 *June* 1965: **Twentieth Annual Northwest Regional Meeting:** *Pacific Northwest Sections of American Chemical Society.* Oregon State University, Corvallis, Ore.

Monday–Friday 14–18 *June* 1965: **Symposium on Molecular Structure and Spectroscopy.** Ohio State University, Columbus, Ohio.

Thursday–Saturday 24–26 *June* 1965: **Conference on Small-Angle X-Ray Scattering.** Syracuse University, Syracuse, N.Y.

Wednesday 29 *September–Friday* 1 *October* 1965: **Twelfth National Vacuum Symposium:** *American Vacuum Society.* Statler-Hilton Hotel, New York City, N.Y.

The Programme Committee solicits the submission of contributed papers for presentation at the Symposium. Abstracts should be submitted by 5 July to the Chairman: R. L. JEPSEN, Varian Associates, 611 Hansen Way, Palo Alto, California 94303, U.S.A.

Contributed papers should report significant results of new and original work, either experimental or theoretical in nature, in an area relating to production, measurement or application of vacuum. Papers dealing with *fundamental* aspects of vacuum production, vacuum measurement and behaviour of materials and surfaces in a vacuum environment are particularly welcome. Papers on new or improved vacuum components and vacuum systems are also welcome provided they are truly technical rather then commercial in nature.

Of special interest this year are papers on such "Space-Related Problems" as friction, sticking and wear under conditions of outer space, and measurements of densities and pressure of various molecular species at high altitudes. Another timely area is electron microscope inspection of microcircuits. Thin films, of course, constitute one of the most important applications of vacuum; it is, therefore, hoped that a large number of good papers will again be contributed in this area.

Following last year's procedure, the *Thin Film Division of the American Vacuum Society* plans to hold a special *Thin Film Division Symposium,* also at the Statler-Hilton Hotel, on September 28, the day preceding the National Vacuum Symposium. This special Symposium will consist exclusively of invited papers on such topics as nucleation and growth, dislocations, and low *energy electron diffraction studies.*

American Society for Testing and Materials has announced that the following publication is now available:

Techniques of Electron Microscopy, Diffraction and Microprobe Analysis: STP 372: 90 + *vi pp. with heavy paper cover.* ($3.75 or $2.60 to ASTM members.)

This presents new techniques and applications of electron microscopy, diffraction and microprobe analysis in research studies. It is well illustrated with photographs, drawings and charts.

UNGARN

8.6. bis 12.6.1965: *Budapest:* Konferenz des wissenschaftlichen Vereins für die Silicatindustrie und der Universität der chemischen Industrie, Veszprém.

Auskunft: Konferenzausschuß Budapest V (Ungarn), Szabadság-tér 17, Haus der Technik, Silikonf.

ERRATA

Volume 12

Page 186, Table I: The heading to the second column should read

$Na_2S_2O_3$,
ml

Page 401: The address of the authors should read *Faculty of Technical and Nuclear Physics.*
Page 405, line 2: for *tartarate* read *tartrate.*
Page 405, Table II: In the footnote read *interfering* for *interferring.*
Page 406, line 5 from bottom of page: For *interferring* read *interfering.*

Talanta, 1965, Vol. 12, p. v. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Some new colorimetric reagents for the determination of platinum metals: Krishna K. Saxena, Kailash N. Munshi and Arun K. Dey. (3 *March* 1965)

A review of organic compounds containing P=S and P(S)SH groups as separation and analytical reagents: Thomas H. Handley. (3 *March* 1965)

Application of activation analysis to the determination of some impurities in nuclear-grade uranium: L. Kosta and G. B. Cook. (4 *March* 1965)

Simultaneous determination of $^{65}_{30}$Zn and $^{12}_{15}$P in shellfish by radiochemical techniques: J. L. Setser and T. C. Rozzell. (8 *March* 1965)

Recent developments in radioactivation analysis: F. Girardi. (8 *March* 1965)

Photometric determination of tervalent gallium, indium and thallium with Xylenol Orange: Chandra D. Dwivedi and Arun K. Dey. (11 *March* 1965)

Precipitation of metal-cupferron complexes from homogenous solution—I: Determination of copper: Arno H. A. Heyn and Natwar G. Dave. (12 *March* 1965)

Precipitation of metal-cupferron complexes from homogenous solution—II: Titanium: Arno H. A. Heyn and Natwar G. Dave. (12 *March* 1965)

Interlingua: A. Gode. (15 *March* 1965)

Thermoanalytical properties of analytical grade reagents—IV: L. Erdey, J. Simon, S. Gál and G. Liptay. (16 *March* 1965)

Determination of magnesium by atomic-absorption spectrophotometry combined with extraction: Masami Suzuki, Masaaki Yanagisawa and Tsugio Takeuchi. (18 *March* 1965)

Determination of plutonium in uranium-plutonium solutions by direct alpha-counting: H. H. Ph. Moeken. (18 *March* 1965)

Effect of dielectric constant on the Rf values of metal ions in some formic acid-alcohol systems: Mohsin Qureshi and Mukhtar A. Khan. (22 *March* 1965)

Spectrophotometric extractive titrations for determination of traces of metals—I: Aftanas Galik. (22 *March* 1965)

Polarography in polymer science: Junji Ukida, Shiron Usami and Tsuguo Kominami. (22 *March* 1965)

Inorganic polarography in organic solvents: Reiji Takahashi. (24 *March* 1965)

On the question of sensitivity evaluation of trace analysis methods: Rudolph Alexander Geitz. (26 *March* 1965)

Reversible indicators for titrations with hypochlorite: R. Belcher, I. El-Khiami and W. I. Stephen. (27 *March* 1965)

Non-destructive activation determination of arsenic in manganese-rich ores and rocks: N. Nenov, H. Popov, T. Tomov and G. Stefanov. (26 *March* 1965)

J. Heyrovský and the development of polarography: P. Zuman. (29 *March* 1965)

Applications of polarography in heterocyclic chemistry: J. Volke. (29 *March* 1965)

Polarography of proteins and its analytical aspects: R. Brdička, M. Březina and V. Kalous. (29 *March* 1965)

Separation and spectrophotometric determination of trace quantities of lithium in high-purity beryllium oxide: R. F. Apple and J. C. White. (1 *April* 1965)

A highly sensitive precipitant for palladium: L. S. Bark and D. Brandon. (2 *April* 1965)

New principle of activation analysis separations—X: Substoichiometric determination of traces of gallium: A. Zeman, J. Růžička and V. Kuvik. (5 *April* 1965)

Talanta, 1965, Vol. 12, p. vii. Pergamon Press Ltd. Printed in Northern Ireland

PUBLICATION RECEIVED

Thin-Layer Chromatography: A Laboratory Handbook: Edited by EGON STAHL. Springer-Verlag, Berlin-Heidelberg-New York, und Academic Press Inc. Publishers, New York and London, 1965. Pp. xv + 553. DM. 68.

General Section. History of the Development of Thin-Layer Chromatography: EGON STAHL; Instruments used in Thin-Layer Chromatography and their Operation: EGON STAHL; Coating Materials for Thin-Layer Chromatography: D. WALDI; Special Techniques: EGON STAHL; Documentation of Thin-Layer Chromatograms: H. GANSHIRT; Quantitative Evaluation of Thin-Layer Chromatograms: H. GANSHIRT; Isotope Techniques: HELMUT K. MANGOLD; Theoretical Aspects of Thin-Layer Chromatography: M. BRENNER *et al.*

Special Section. Introduction: EGON STAHL; Aliphatic Lipids: HELMUT K. MANGOLD; Terpene Derivatives, Essential Oils, Balsams, and Resins: EGON STAHL and H. JORK; Vitamins: H. R. BOLLIGER; Steroids (Sterols; Pregnane-, Androstane-, and Estrane-Compounds; Bile Acids and Cardiac Glycosides): D. WALDI; Organic Bases: D. WALDI and EGON STAHL; Pharmaceutical Products: H. GANSHIRT; Thin-Layer Chromatography in Clinical Diagnosis and Pharmacology: D. WALDI; Synthetic Organic Materials: H. GANSHIRT, D. WALDI and EGON STAHL; Hydrophillic Constituents of Plants: EGON STAHL and P. J. SCHORN; Amino Acids and Derivatives: M. BRENNER, A. NIEDERWIESER and G. PATAKI; Nucleic Acids and Nucleotides: HELMUT K. MANGOLD; Sugars and Derivatives: EGON STAHL and U. KALTENBACH; Thin-Layer Chromatography of Inorganic Ions: H. SEILER; Spray Reagents for Thin-Layer Chromatography: D. WALDI; Terminology of Thin-Layer Chromatography (English-German-French): HELLUT K. MANGOLD and M. BRENNER; Commercial Suppliers.

Conversion table for Rf into Rm and *vice versa*; Author Index; Subject Index.

PUBLISHER'S ANNOUNCEMENT

REPRINTS OF REVIEW PAPERS

Reprints of the following reviews published in Talanta are available from Journals Department, Pergamon Press Ltd., Headington Hill Hall, Oxford, England, at 7s. or $1 per copy, on a cash with order basis only:

"Precipitation of Metal Chelates from Homogeneous Solution" by F. H. Firsching.

"Recent Developments in the Ring Oven Technique" by H. Weisz.

"Adsorption Indicators in Precipitation Titrations" by R. C. Mehrotra and K. N. Tandon.

"Radiometric Titrations" by T. Braun and J. Tölgyessy.

"Recent Uses of Liquid Ion Exchangers in Inorganic Analysis" by H. Green.

"Applications of Neutron and Electron Magnetic Resonance in Analytical Chemistry" by B. C. Flockhart and R. C. Pink.

Salt Research and Industry

Official publication of the Central Salt and Marine Chemicals Research Institute Bhavnagar.

This new quarterly journal maintains a close liaison between research workers for the Central Salt and Marine Chemicals Research Institute and scientists, technologists, industrialists, salt manufacturers and others engaged in the salt industry. The main purpose of the journal is to inform the salt manufacturers of the research work carried out in the Institute, to create interest in the recovery of by-products of salt, and to encourage the use of new and more efficient methods of salt manufacture.

Salt Research and Industry publishes papers on all aspects of the production of salt and marine chemicals, the conversion of sea water into fresh water for drinking or irrigation purposes, the cultivation and utilization of marine algae, chemical engineering laboratory studies, and plant development and design.

Typical papers from previous issues:

Activities of the CSMCRI and main achievements during the period 1954-64; Origin of salt—I, theories; Growth pattern of salt industry in India—I, survey; Mechanization in salt farms; Manufacture of potash fertilizers; Magnesium chemicals in industry; Marine algal cultivations; General problems of salt and by-products industry; Mechanical harvesting of salt; Methods of analysis for salt industry; Salt and dietetics; Methods of controlling algal growths in sea water for salt and chemical industries, a review; Proteins from ulva.

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