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WHAT'S NEW FROM B.D.H.?

SODIUM HYDRIDE 50% DISPERSION IN OIL

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A dispersed form of sodium hydride consisting of 1-20 micron cubic crystals in mineral oil. The moist grey highly reactive powder is simple to handle, reactions are speeded up, no great excess is normally required, and side reactions are minimised. Using the dispersion, sodio derivatives of many compounds can be prepared in high yield. It can advantageously replace the usual form of sodium hydride in, for example, Claisen acylations and carboethoxylations of esters and ketones¹; in preparing phenates²; and as a condensing agent in Stobbe condensations³.

1. Swamer, F. W. and Hauser, C. R., *J. Amer. Chem. Soc.*, 1950, 72, 1352-6

2. Wheatley, N. B. and Cheney, L. C., *J. Amer. Chem. Soc.*, 1949, 71, 64-6; 3795-7

3. Daub, G. H. and Johnson, W. S., *J. Amer. Chem. Soc.*, 1950, 72, 501-4

POTASSIUM HYDROGEN PHTHALATE pH STANDARD

*Certified by the National
Chemical Laboratory*

The primary pH Standard¹ is an M/20 aqueous solution of pure potassium hydrogen phthalate, which has been assigned a pH value of 4.000 at 15°C. Potassium hydrogen phthalate specially purified by B.D.H. has been tested as a Standard by the N.C.L. at four different temperatures and has been certified as satisfactory; the results of the tests are well within the limits imposed by B.S. 1647:1961.

Each 100g pack of the colourless crystalline material carries a leaflet describing the Laboratory's methods of testing, its results, and the criteria it has applied. Further copies of the leaflet will be sent free on request.

1. British Standard 1647: 1950 and 1961

8-ACETOXY-QUINOLINE

A source of oxine

The reagent provides a convenient method for preparing 8-hydroxy-quinoline (oxine) *in situ* in homogeneous aqueous solutions containing metal ions. The resulting complexes have superior physical characteristics when compared with those obtained directly from oxine, larger, better-developed and more easily filterable crystalline precipitates being formed.¹ Gravimetric determinations using 8-acetoxy-quinoline have been successfully made on thorium, aluminium, uranium, magnesium and other metals.

1. Salesin, E. D. and Gordon, L., *Talanta*, 1960, 4, 75-7

4-(p-NITRO-BENZYL)- PYRIDINE

A reagent for phosgene

A rapid field-test¹ for phosgene is carried out by drawing 120 ml samples of air through filter paper impregnated with a solution of 2% 4-(p-nitro-benzyl)-pyridine and 4% N-benzyl-aniline in benzene, the red stain which appears when COCl₂ is present being compared with suitable standards. The test is conveniently used in conjunction with the Lovibond Nessleriser and Disc 6/18, which contains colour standards covering the range 0.25 to 10 p.p.m. of phosgene. All the materials for the test are supplied by B.D.H.

1. Dixon, B. E. and Hands, G. C., *Analyst*, 1959, 84, 463-4



THE BRITISH DRUG HOUSES LTD.

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SUMMARIES FOR CARD INDEXES

Determination of cobalt(II) ions by a differential spectrophotometric method: A. PÁLL, G. SVEHLA and L. ERDEY, *Talanta*, 1964, **11**, 1383. (Institute for General Chemistry, Technical University of Budapest, XI. Gellértér 4, Budapest, Hungary.)

Summary—Cobalt(II) ions can be determined in the form of perchlorate by a differential spectrophotometric method, after evaporating the cobalt samples with perchloric acid to the production of perchloric acid fumes. From the absorption spectrum of cobalt(II) perchlorate the peak occurring at 19600 cm^{-1} ($511\text{ m}\mu$) is chosen for the determination. By the systematic investigation of optimum concentration limits it has been shown that if a solution containing 12 g/litre of cobalt is used as a reference, the concentration determination can be carried out with an error less than 1%, while the corresponding photometric error decreases to less than 0.1%. The effects of some foreign ions have been investigated; chromium, if present in the trivalent state, causes high positive errors. Other metal ions examined have no significant effect.

The determination of sodium, potassium, magnesium, manganese and calcium in cement by atomic-absorption spectrophotometry: TSUGIO TAKEUCHI and MASAMI SUZUKI, *Talanta*, 1964, **11**, 1391. (Institute of Analytical Chemistry, Faculty of Engineering, Nagoya University, Nagoya, Japan.)

Summary—Various aspects of the determination of sodium, potassium, magnesium, manganese and calcium in cement by atomic-absorption spectrophotometry are described. For the determination of sodium, potassium and magnesium, both the calibration curve method and the addition method were found suitable because of the linear relationship between absorption and concentration. For the determination of manganese and calcium, the calibration curve method was found suitable. The calibration curves for sodium and potassium must be prepared to contain the same concentration of calcium as the analysed samples. The method is rapid, and no preliminary separations are necessary. The precision for the determination of sodium, potassium, magnesium and manganese is satisfactory, but is insufficient for calcium because of the large calcium content of cement.

Chelating properties of the chelating ion exchanger Dowex A-1: H. LOEWENSCHUSS and G. SCHMUCKLER, *Talanta*, 1964, **11**, 1399. (Department of Chemistry, Technion-Israel Institute of Technology, Haifa, Israel.)

Summary—The properties and behaviour of the chelating ion exchanger Dowex A-1 have been studied when in contact with an aqueous solution containing metal ions complexed with aminocarboxylic ligands. The stability constants of the metal ion complexes with the resin have been determined as well as the structure of the complexes formed by the metal ions, the resin and the ligands in the solution. Dowex A-1 behaves as a solid complexing agent and forms stable 1:1 complexes with metal ions.

СКОРОСТЬ РЕАКЦИИ СТЕКЛЯНЫХ ЭЛЕКТРОДОВ:

G. A. RESCHNITZ, *Talanta*, 1964, **11**, 1467.

Резюме—Повторенное испытание ответа катионо-чувствительных стеклянных электродов на быстрые перемены концентрации дало характеристичное время ответа 1,5–4,0 сек. и указывает что такими электродами возможно пользоваться для непрерывного анализа или для изучения скорости реакции.

**ОПРЕДЕЛЕНИЕ НАТРИЯ, КАЛИЯ, МАГНИЯ,
МАРГАНЦА И КАЛЬЦИЯ В ЦЕМЕНТЕ МЕТОДОМ
АТОМНОГО ПОГЛОЩЕНИЯ:**

TSUGIO TAKEUCHI and MASAMI SUZUKI, *Talanta*, 1964, **11**, 1391.

Резюме—Исследовалось влияние различных факторов на определение в цементе натрия, калия, магния, марганца и кальция методом атомного поглощения. Для определения натрия, калия и магния могут применяться как метод стандартной кривы, так и метод добавки, потому что в обоих методах существует линейное отношение между поглощением и концентрацией. Для определения марганца и кальция авторы предлагают метод стандартной кривы. Стандартные кривы для натрия и калия должны определиться в присутствии концентрации кальция, соответствующей концентрацией в пробе. Метод быстрый и не изыскивает предварительные разделения. Точность метода удовлетворительна для натрия, калия, магния и марганца но не довольна для кальция, вследствие большой концентрации кальция в цементе.

**КОМПЛЕКСООБРАЗОВАТЕЛЬНЫЕ СВОЙСТВА
ДАУЕКСА А-1:**

H. LOEWENSCHUSS and G. SCHMUCKLER, *Talanta*, 1964, **11**, 1399.

Резюме—Исследованы свойства комплексообразующей ионообменной смолы в контакте с водным раствором ионов металла, связанных с аминокарбоксильным лигандом. Были определены константы устойчивости металлов со смолой, как и строение комплекса, состоящегося из металла, смолы и лиганда в растворе. Дауекс А-1 ведет себя как твердый комплексообразователь и творит устойчивые комплексы с металлами в отношении 1:1.

A study of the oxidation of manganese (II) and chromium (III) ions by silver (II) oxide: C. P. LLOYD and W. F. PICKERING; *Talanta*, 1964, **11**, 1409. (Department of Chemistry, Newcastle University College, Tighes Hill, N.S.W., Australia.)

Summary—A study has been made of the oxidation of manganese (II) and chromium (III) solutions by silver (II) oxide in perchloric acid medium. Both the efficiency and the rate of the oxidation process were found to vary with the concentration of reductant, the amount of AgO added, the temperature, the acidity and the concentration of univalent silver ions in the solution. The inefficiency of the oxidation process can be attributed to the simultaneous formation of oxygen. The results are discussed in terms of a possible reaction mechanism, and the optimum conditions for oxidations using AgO are indicated.

Some problems in the analysis of gaseous decomposition products: A critical evaluation: PAUL D. GARN, *Talanta*, 1964, **11**, 1417. (Department of Chemistry, The University of Akron, Akron, Ohio, U.S.A.)

Summary—Whether the analysis of effluent gases during thermal decompositions is used to elucidate the progress or the mechanism of the decompositions, or to characterise the specimen, certain problems must be dealt with. These problems, involving heating, the analysis of the products, and the compromises which must be made in simultaneous measurements, are discussed.

Quenchofluorometric analysis for fluoranthenic hydrocarbons in the presence of other types of aromatic hydrocarbon: E. SAWICKI, T. W. STANLEY and W. C. ELBERT, *Talanta*, 1964, **11**, 1433. (Laboratory of Engineering and Physical Sciences, Division of Air Pollution, Robert A. Taft Sanitary Engineering Center, Public Health Service, U.S. Department of Health, Education and Welfare, Cincinnati, Ohio, U.S.A.)

Summary—In this first paper of a series, a new analytical tool is introduced for the analysis of fluorescent molecules—quenchofluorescence analysis. This field of research will have far-reaching ramifications in organic trace analysis. Analytical use is made of the quenching effect in spectrophotofluorometry. Compounds such as anthracene, phenanthrene, pyrene, benz(*a*)anthracene, benzo(*a*)pyrene, perylene, *etc.*, have been found to be non-fluorescent in nitromethane solution, but hydrocarbons containing the fluoranthenic ring are fluorescent. Use has been made of this phenomenon in characterising fluoranthene and benzo(*k*) fluoranthene in airborne particulates, following column chromatography. The phenomenon has also been used in thin-layer chromatography, directly on the plate.

Some rather unusual chemical analyses: JAMES O. HIBBITS and SILVE KALLMANN, *Talanta*, 1964, **11**, 1443. (General Electric Company, Nuclear Materials and Propulsion Operation, Cincinnati 15, Ohio, U.S.A.)

Summary—Some rather unusual chemical analyses are described. A typical example is the determination of a few μg of one element in a sample composed essentially of the elements listed in the periodic table. This somewhat bizarre sample is a solution containing 10 mg each of about seventy different elements.

**ИССЛЕДОВАНИЕ ОКИСЛЕНИЯ ОКИСЬЮ СЕРЕБРА(II)
ИОНОВ МАРГАНЦА(II) И ХРОМА(III):**

C. P. LLOYD and W. F. PICKERING, *Talanta*, 1964, **11**, 1409.

Резюме—Было исследовано окисление окисью серебра(II) растворов марганца(II) и хрома(III) в хлорноокислой среде. Обнаружилось, что выход и скорость процесса окисления меняется с концентрацией восстановителя, прибавленным количеством Ag_2O , температурой, кислотностью и концентрацией ионов одновалентного серебра в растворе. Неэффективность процесса окисления можно приписать одновременному образованию кислорода. Результаты обсуждаются на основании предложенного механизма реакции и приносятся условия для окисления с Ag_2O .

**НЕКОТОРЫЕ ПРОБЛЕМЫ В АНАЛИЗЕ ГАЗО-
ОБРАЗНЫХ ПРОДУКТОВ РАЗЛОЖЕНИЯ.
КРИТИЧЕСКОЕ ОБСУЖДЕНИЕ:**

PAUL D. GARN, *Talanta*, 1964, **11**, 1417.

Резюме—Обсуждаются проблемы являющиеся в анализе газов, вытекающих при тепловых разложениях; цель этого анализа может быть исследование механизма разложения или характеризование пробы. Эти проблемы включают нагревание, анализ продуктов и компромиссы, необходимы в одновременных измерениях.

**ОПРЕДЕЛЕНИЕ ФЛУОРАНТЕНОВЫХ УГЛЕВО-
ДОРОДОВ В ПРИСУТСТВИИ ДРУГИХ АРОМАТИ-
ЧЕСКИХ УГЛЕВОДОРОДОВ МЕТОДОМ ГАШЕНИЯ
ФЛУОРЕСЦЕНЦИИ:**

E. SAWICKI, T. W. STANLEY and W. C. ELBERT, *Talanta*, 1964, **11**, 1433.

Резюме—В этой статье—первой из ряда статей—представляется новый метод для анализа флуоресцирующих молекул: метод гашения флуоресценции, который представляет аналитическое применение эффекта гашения в спектрофотометрии. Было обнаружено что углеводороды содержащие флуорантеновое кольцо флуоресцируют в нитрометановом растворе, пока антрацен, фенантрен, пирен, бензо(а)-антрацен, бензо(а)пирен, перилен и др. не флуоресцируют. Это явление применено для характеризования флуорантена и бензо(к)флуорантена в частицах, находящихся в воздухе, после хроматографии в колонне. Явление тоже применено в танкослойной хроматографии, прямо на пластинке.

**НЕКОТОРЫЕ НЕОБЫКНОВЕННЫЕ ХИМИЧЕСКИЕ
АНАЛИЗЫ:**

JAMES O. HIBBITS and SILVE KALLMAN, *Talanta*, 1964, **11**, 1443.

Резюме—Описывается ряд несколько необыкновенных химических анализов. Как типичный пример приводится определение нескольких микрограммов одного элемента в пробе состоящейся в сущности из всех элементов периодической системы. Эта проба содержит 10 мг от каждого из 70 элементов.

Studies of the fire assay for platinum metals by lead collection: K. C. AGRAWAL and F. E. BEAMISH, *Talanta*, 1964, **11**, 1449. (University of Toronto, Department of Chemistry, Toronto 5, Ontario, Canada.)

Summary—A fire-assay procedure for determining platinum, palladium, rhodium or iridium in the nitric acid parting solution from a lead button is described. Palladium is the only metal which is completely attacked by the parting solution; traces of platinum and rhodium are also dissolved. The presence of copper in the lead button has been found to encourage the dissolution of both platinum and iridium in the nitric acid parting solution; rhodium remains unaffected. Ion-exchange and precipitation procedures for separating palladium from lead are also included. Efforts have been made to identify the source of iridium loss which is a characteristic of classical fire assay collections.

A new class of fluorescent adsorption indicators; A. BASIŃSKI and K. KICIAK, *Talanta*, 1964, **11**, 1459. (Institute of Physical Chemistry, Copernicus University, Toruń, Poland.)

Summary—Oxacyanine and thiacyanine dyes have been found to act as fluorescent adsorption indicators in the cyanometric titration of silver halides.

Use of masking agents in chelatometric titrations—IV: Dimercaptosuccinic acid: T. MEKADA, K. YAMAGUCHI and K. UENO, *Talanta*, 1964, **11**, 1461. (Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Fukuoka, Japan.)

Summary—Dimercaptosuccinic acid has been examined as a masking agent in EDTA titrations. At pH 6 it is possible to determine zinc in the presence of cadmium, copper(II) and mercury(II). At pH 10 most bivalent cations except for the alkaline earth metals can be masked.

A specific method for the determination of trace amounts of titanium: J. O. HIBBITS, S. KALLMANN, W. GIUSTETTI and H. K. OBERTHIN, *Talanta*, 1964, **11**, 1464. (Nuclear Materials and Propulsion Department, General Electric Company, Cincinnati 15, Ohio, U.S.A.)

Summary—A method is presented which is specific for the determination of trace amounts of titanium. Titanium is precipitated with cupferron using zirconium as a collector. Further separation from interfering elements is made by anion exchange and precipitation with sodium hydroxide using iron as a collector. The determination is completed colorimetrically after extraction of the titanium-thiocyanate complex with a solution of tri-n-octylphosphine oxide in cyclohexane. The method is accurate to within $\pm 5\%$ (relative) or $\pm 0.75 \mu\text{g}$ of titanium, whichever is greater.

ОПРЕДЕЛЕНИЕ СОДЕРЖАНИЯ ПЛАТИНОВЫХ
МЕТАЛЛОВ ПУТЕМ СОБИРАНИЯ СВИНЦА:

K. C. AGRAWAL and F. E. BEAMISH, *Talanta*, 1964, 11, 1449.

Резюме—Описывается метод для определения платины, палладия, родия или иридия в азотнокислом разделительном растворе свинцового королька. Палладий единственный металл полностью атакован разделительным раствором; следы платины и родия тоже растворяются. Присутствие меди в свинцовом корольке повышает растворимость платины, и иридия в азотнокислом растворе; родий не реагирует. Работа тоже содержит процедуры для отделения палладия от свинца помощью осаждения и ионного обмена. Пыталось открыть причину потери иридия, которая характеризует классические процедуры.

НОВЫЙ КЛАСС ФЛУОРЕСЦИРУЮЩИХ
АДСОРБЦИОННЫХ ИНДИКАТОРОВ:

A. BASINSKI and K. KISIAK, *Talanta*, 1964, 11, 1459.

Резюме—Красители из классов оксаанинов и тиацианинов были использованы как флуоресцирующие адсорбционные индикаторы для цианометрического титрования галогенидов серебра.

ПРИМЕНЕНИЕ МАСКИРУЮЩИХ АГЕНТОВ ПРИ
КОМПЛЕКСОМЕТРИЧЕСКИХ ТИТРОВАНИЯХ—IV:
ДИМЕРКАПТОЯНТАРНАЯ КИСЛОТА:

TORU MUKADA, KOICHI YAMAGUCHI and KEIHEI UENO, *Talanta*, 1964, 11, 1461.

Резюме—Исследовано применение димеркаптоянтарной кислоты как маскирующего агента в титрованиях с ЭДТА. Пользуясь этим реагентом при pH 6 возможно определить цинк(II) в присутствии кадмия(II), меди(II) и ртути(II). При pH 10 этот реагент маскирует большинство двухвалентных катионов, исключая ионы щелочных земель.

ИЗБИРАТЕЛЬНЫЙ МЕТОД ДЛЯ ОПРЕДЕЛЕНИЯ
ТИТАНА:

JAMES O. HIBBITS, SILVE KALLMAN, WILLIAM GIUSTETTI and HANS K. OVERTHIN, *Talanta*, 1964, 11, 1464.

Резюме—Представлен метод для определения следовых количеств титана. Титан осаждается купферроном, пользуясь цирконием как коллектором. Дальнее отделение от мешающих элементов получается ионным обменом и осаждением с гидроксидом натрия, пользуясь железом как коллектором. Роданидный комплекс титана экстрагируется раствором окиси три-*n*-октилфосфина в циклогексане. Точность метода $\pm 5\%$ относительно или $0,75 \mu\text{г}$ титана.

Summaries for card indexes

Response rates of cation-sensitive glass electrodes: G. A. RECHNITZ, *Talanta*, 1964, **11**, 1467. (Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, U.S.A.)

Summary—A re-evaluation of the response of cation-sensitive glass electrodes to rapid concentration changes indicates typical response times in the 1.5–4.0 sec range and suggests that such electrodes might be used for continuous analyses or for reaction rate studies.

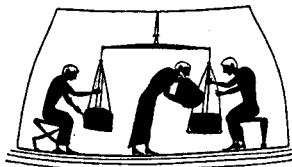
ОПРЕДЕЛЕНИЕ КОБАЛЬТ-ИОНОВ
ДИФФЕРЕНЦИАЛЬНЫМ СПЕКТРОФОТОМЕТ-
РИЧЕСКИМ МЕТОДОМ:

A. PÁLL, G. SVENLA and L. ERDEY, *Talanta*, **11**, 1383.

Резюме—Ионы кобальта(II) определяются дифференциальным спектрофотометрическим методом в форме перхлората после испарения пробы с хлорной кислотой всё до появления паров хлорной кислоты. Для определения кобальта выбран максимум поглощения при 19600 см^{-1} (511 мкм). Систематическим исследованием оптимальной концентрации авторам удалось доказать что ошибка при определении концентрации меньше 1% а соответствующая фотометрическая ошибка менее 0,1% если стандартный раствор содержит 12 г/л кобальта. При исследовании влияния некоторых других металлов оказалось что трехвалентный хром вызывает высокие результаты. Ионы других металлов имеют только небольшое влияние.

TALANTA

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NOTES FOR CONTRIBUTORS

1. General

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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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DETERMINATION OF COBALT(II) IONS BY A DIFFERENTIAL SPECTROPHOTOMETRIC METHOD

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Summary—Cobalt(II) ions can be determined in the form of perchlorate by a differential spectrophotometric method, after evaporating the cobalt samples with perchloric acid to the production of perchloric acid fumes. From the absorption spectrum of cobalt(II) perchlorate the peak occurring at 19600 cm^{-1} ($511\text{ m}\mu$) is chosen for the determination. By the systematic investigation of optimum concentration limits it has been shown that if a solution containing 12 g/litre of cobalt is used as a reference, the concentration determination can be carried out with an error less than 1%, while the corresponding photometric error decreases to less than 0.1%. The effects of some foreign ions have been investigated; chromium, if present in the trivalent state, causes high positive errors. Other metal ions examined have no significant effect.

THE use of high-performance spectrophotometers permits of a desirable increase in the accuracy of analytical determinations. In particular, differential spectrophotometry promises the reduction of errors to such an extent that even ions which are present as main constituents in samples can be determined with adequate accuracy. Numerous differential spectrophotometric methods have already been described by various authors, among which determinations of copper,¹ nickel,² dichromate and permanganate,³ titanium,⁴ uranium,^{5,6} vanadium⁷ and phosphate⁸ are the most widely used. The present investigation was to find the best experimental conditions for the determination of cobalt in the form of cobalt(II) perchlorate. From the point of view of differential spectrophotometric methods, the measurement of the optical densities of metal perchlorates are very suitable, partly because perchlorates generally do not form complexes which cause deviation from Beer's law, and partly because perchlorates can easily be prepared by simple evaporation with perchloric acid.

EXPERIMENTAL

Reagents

Cobalt(II) perchlorate solution, containing 50.00 mg/ml of cobalt, was prepared by dissolving 246.904 g of analytically pure cobalt(II) nitrate hexahydrate in water to which 350 ml of 60% perchloric acid were added, and cautiously evaporating the mixture to the appearance of white perchloric acid fumes. The solution was then diluted with water to exactly 1 litre. The cobalt content of the solution was checked by gravimetric methods.

This was used as a stock solution for the preparation of comparison standards. Because no marked effect on the optical densities was found if the concentration of perchloric acid was changed over a wide range, dilutions from the stock solution were simply made by water.

Apparatus

The absorption spectra of the metal perchlorates were obtained by a Unicam SP 700 spectrophotometer, equipped with a recorder presenting transmittance *vs.* wave numbers. One-cm silica cells were used, and spectra were recorded between 50×10^3 and $4 \times 10^3\text{ cm}^{-1}$ wave numbers.

Optical densities were measured with a Hilger Uvispec spectrophotometer. Two 1-cm silica cells were used systematically, one always containing the reference solution, the other being the one to be measured.

RESULTS AND DISCUSSION

Absorption spectra

The transmittances of accurately prepared metal perchlorate solutions, containing 10 g of metal ion in 1 litre of solution (10 mg/ml), were measured against water. Fig. 1 shows the absorption spectrum of cobalt(II) perchlorate. The curve shows a characteristic maximum at 19600 cm^{-1} ($511\text{ m}\mu$). This wavelength was used for the optical density measurements, where the specific absorbance of cobalt^{II} ions is $7.9 \times 10^{-2}\text{ litre.g}^{-1}\text{.cm}^{-1}$. Similarly, the absorption spectra of the perchlorates of those metal ions which often occur with cobalt were checked carefully for interference.

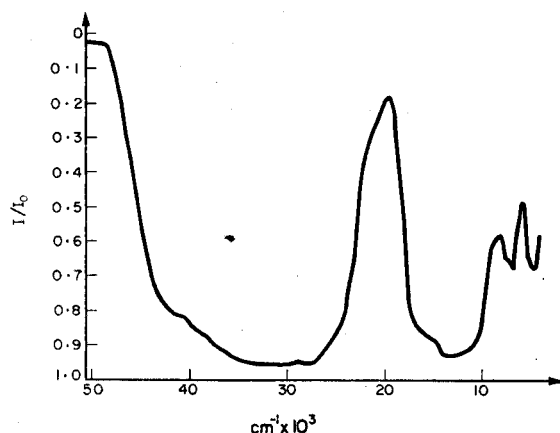


FIG. 1.—Absorption spectrum of cobalt(II) perchlorate (10 g of Co^{II} /litre)

The absorption spectra of the perchlorates of nickel(II), iron(II), copper(II) and chromium(III) are shown in Figs. 2, 3, 4 and 5 respectively.

By comparing these spectra it can be seen that the absorbances of nickel(II), iron(II) and copper(II) perchlorates at 19600 cm^{-1} are very low, and therefore there are no serious interferences to be expected in their presence. Chromium(III) perchlorate, however, shows marked absorption at this wavelength, and therefore a marked interference from chromium(III) is to be expected in determinations.

Optimum concentration limits

The determination of the optimum concentration limits was made by carrying out a series of sets of optical density measurements and calculating the corresponding percentage errors of the concentration determinations.⁹ The region showing lowest errors was chosen as the most suitable one.

A set of solutions was prepared, containing 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36 and 38 g of cobalt per litre. Five sets of experiments were made. As reference solutions water (concentration = 0) and cobalt(II) perchlorate solutions containing 6, 12, 18 and 24 g of cobalt per litre were chosen. Optical densities were measured in all cases six times (including refilling of the cells and readjustment of the instrument). The means of six readings are presented in Table I.

In each set the optical densities, when plotted against concentrations, yield linear curves. Using the method of least squares, the equations of the best linear curves fitting the experimental points were determined, together with the standard deviations of the intercept and the slope. These equations are summarised in Table II.

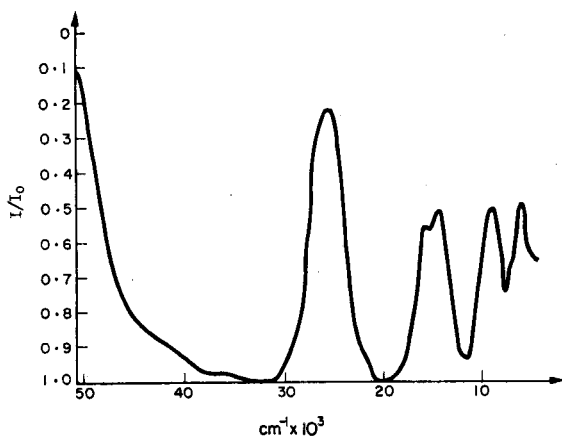


FIG. 2.—Absorption spectrum of nickel(II) perchlorate (10 g of Ni^{II} /litre)

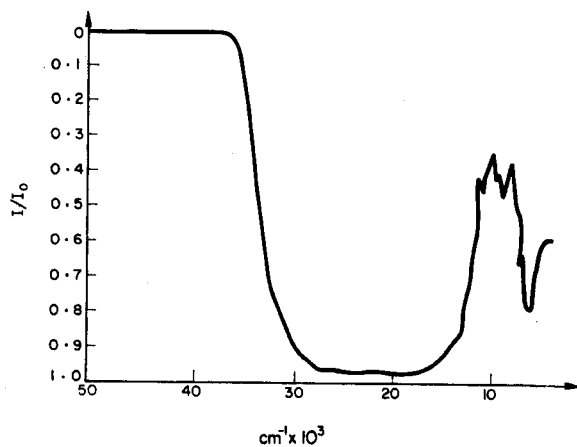


FIG. 3.—Absorption spectrum of iron(II) perchlorate (10 g of Fe^{II} /litre)

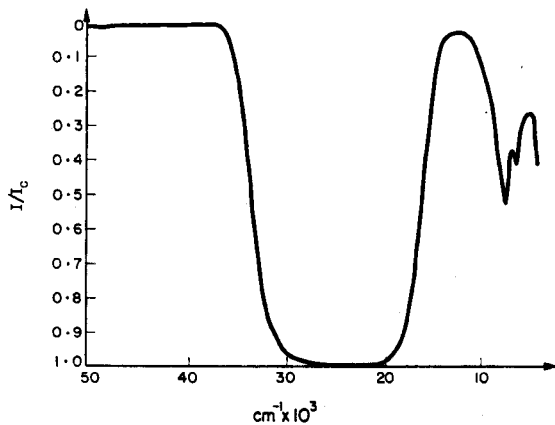


FIG. 4.—Absorption spectrum of copper(II) perchlorate (10 g of Cu^{II} /litre)

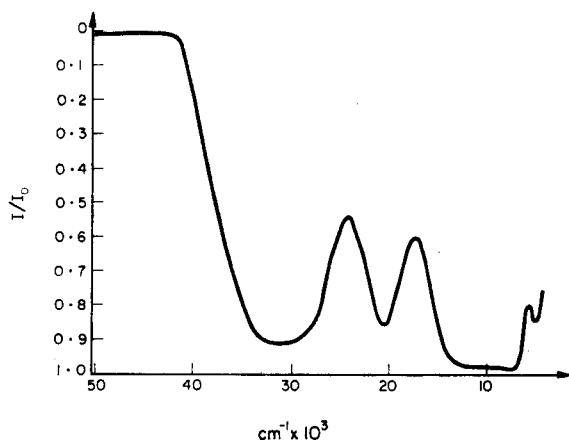


FIG. 5.—Absorption spectrum of chromium(III) perchlorate (1 g of Cr^{III} /litre)

TABLE I.—OPTICAL DENSITIES OF COBALT(II) PERCHLORATE SOLUTIONS

Concentration of cobalt, g/litre	Optical density measured against solutions having concentrations of cobalt, g/litre				
	0	6	12	18	24
0	0.0000				
2	0.168				
4	0.334				
6	0.506	0.0000			
8	0.674	0.1676			
10	0.816	0.3075			
12	1.045	0.5180	0.0000		
14	1.194	0.6825	0.1680		
16	1.372	0.8600	0.3393		
18	1.562	1.0440	0.4958	0.0000	
20	1.738		0.6720	0.1649	
22			0.8272	0.3244	
24			1.0030	0.4904	0.0000
26			1.1900	0.6865	0.1928
28			1.3625	0.8405	0.3537
30			1.5525	0.9604	0.5290
32					0.6778
34					0.8320
36					0.9835
38					1.1484

TABLE II.—CORRELATIONS BETWEEN CONCENTRATION AND OPTICAL DENSITY

Concentration of the reference solution, C_{ref} , g/litre	Best linear curve fitting the experimental points, $E = ac + b$	Standard deviation of	
		Intercept S_a	Slope S_b
0	$0.0874 C + 0.0206$	$\pm 1.14 \times 10^{-2}$	$\pm 9.20 \times 10^{-4}$
6	$0.0873 C - 0.5362$	$\pm 5.01 \times 10^{-2}$	$\pm 3.97 \times 10^{-3}$
12	$0.0855 C - 11.0343$	$\pm 8.05 \times 10^{-2}$	$\pm 3.7 \times 10^{-3}$
18	$0.0820 C - 1.4736$	$\pm 4.39 \times 10^{-2}$	$\pm 1.81 \times 10^{-3}$
24	$0.0807 C - 1.9149$	$\pm 3.30 \times 10^{-2}$	$\pm 1.10 \times 10^{-3}$

TABLE III.—ERRORS OF COBALT DETERMINATIONS BY DIFFERENTIAL SPECTROPHOTOMETRIC METHODS

Cobalt(II), g/litre	Photometric error,			Total error, $\frac{S_c}{c} \times 100,$ %
	$\frac{S_B}{E-b} \times 100,$ %	$\frac{S_b}{E-b} \times 100,$ %	$\frac{S_a}{a},$ %	
Measured against water ($C_{ref} = 0$)				
2	1.36	6.54		8.95
4	0.22	3.27		4.54
6	0.15	2.18	1.05	3.38
8	0	1.63		2.69
10	0.11	1.31		2.47
12	0.14	1.09		2.28
14	0.25	0.93		2.24
Measured against $C_{ref} = 6$ g of Co per litre of solution				
8	0.03	7.18		11.76
10	0.06	5.75		10.36
12	0.02	4.79	4.55	9.37
14	0.06	4.11		8.71
16	0.07	3.59		8.21
18	0.07	3.19		7.80
Measured against $C_{ref} = 12$ g of Co per litre of solution				
14	0.04	0.67		1.15
16	0.03	0.59		1.04
18	0.02	0.52		0.98
20	0.02	0.47	0.43	0.92
22	0.08	0.43		0.94
24	0.07	0.39		0.89
26	0.05	0.36		0.84
Measured against $C_{ref} = 18$ g of Co per litre of solution				
20	0.04	2.68		4.92
22	0.21	2.43		4.85
24	0.03	2.23	2.21	4.47
26	0.06	2.06		4.32
28	0.07	1.91		4.19
30	2.29	1.78		6.28
Measured against $C_{ref} = 24$ g of Co per litre of solution				
26	0.04	0.04		5.06
28	0.04	1.46		5.14
30	0.09	1.36	1.38	5.25
32	0.18	1.28		5.41
34	0.21	1.20		5.54
36	0.39	1.14		5.81
38	0.25	1.08		5.77

For all the sets of experiments the errors were then calculated, as described elsewhere.⁹ It was there pointed out that the error of concentration determination by a differential spectrophotometric method depends on the measured optical density (*i.e.*, on the concentration itself) and can be expressed by the following equation:

$$\frac{S_C}{C} \times 100 = \frac{S_E}{E - b} \times 100 + \frac{S_b}{E - b} \times 100 + \frac{S_a}{a} \times 100.$$

Simplifications arising from the use of cells of 1 cm in length are included in this expression. Here S_b and S_a are the standard deviations of the intercept and slope,

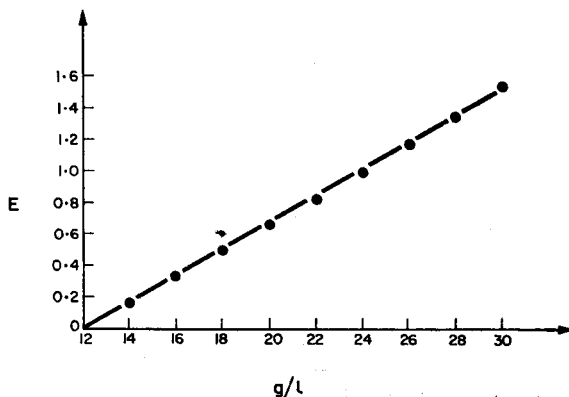


FIG. 6.—Calibration curve for cobalt determination ($E_{\text{ref}} = 0.975$)

respectively, while the value S_E is the standard deviation of the optical density measurements. The value $\frac{S_E}{E - b} \times 100$ is the so-called photometric error; for the details of its calculation see the earlier paper.⁹ The results of the error calculations are shown in Table III. The best results can be obtained using a solution containing 12 g of cobalt per litre as a reference. In this case the total error of the method is somewhat lower than 1%, while the "photometric error," *i.e.*, the coefficient of variation of the optical density measurement, is generally lower than 0.1%. The calibration curve is shown in Fig. 6.

Effect of foreign ions

Various metal ions (5, 10, 15 and 20 g per litre) were added to solutions containing 22 g of cobalt(II) per litre. The optical densities of the resulting solutions were measured against a reference solution containing 12 g per litre of cobalt.

The results of these measurements, together with the errors caused by the metal ions, are presented in Table IV. As may be seen from these results, the investigated metal ions reduce the optical density, causing about a 1% negative error in the concentration measurement. This excludes chromium which, as pointed out earlier, causes a very high positive error; this can be eliminated, however, by the oxidation of chromium to chromate. A further report will be given later on this, and on the differential spectrophotometric determination of chromium.

TABLE IV.—EFFECT OF FOREIGN ION

Ion	Concentration of foreign ion, g/litre	Optical density	Cobalt concentration, g/litre		Error caused by the ion	
			True value	Measured value	g/litre	%
Cr ³⁺	5	1.136	22.00	25.38	+3.38	+15.3
	10	1.518	22.00	20.84	+7.84	+35.6
	15	1.944	22.00	34.83	+12.83	+58.3
	20	2.245	22.00	38.35	+16.35	+74.3
Ni ²⁺	5	0.792	22.00	21.35	-0.65	-2.95
	10	0.820	22.00	21.68	-0.32	-1.45
	15	0.840	22.00	21.91	-0.09	-0.41
	20	0.820	22.00	21.68	-0.32	-1.45
Cu ²⁺	5	0.792	22.00	21.35	-0.65	-2.95
	10	0.776	22.00	21.17	-0.83	-3.77
	15	0.776	22.00	21.17	-0.83	-3.77
	20	0.814	22.00	21.61	-0.39	-1.77
Mn ²⁺	5	0.826	22.00	21.75	-0.25	-1.13
	10	0.831	22.00	21.81	-0.19	-0.86
	15	0.844	22.00	21.96	-0.04	-0.18
	20	0.835	22.00	21.85	-0.15	-0.68
Fe ²⁺	5	0.794	22.00	21.38	-0.62	-2.81
	10	0.824	22.00	21.73	-0.27	-1.22
	15	0.816	22.00	21.63	-0.37	-1.68
	20	0.828	22.00	21.77	-0.23	-1.04
Fe ³⁺	5	0.784	22.00	21.26	-0.74	-3.36
	10	0.823	22.00	21.71	-0.29	-1.31
	15	0.812	22.00	21.59	-0.41	-1.86
	20	0.832	22.00	21.82	-0.18	-0.81

Procedure

Dissolve a sample, containing about 1.5–2.5 g of cobalt in 50 ml of perchloric acid (1:3). If this cannot be done, dissolve the sample in any other way and evaporate the solution together with 50 ml of perchloric acid (1:3) until white perchloric acid fumes appear. Allow to cool, transfer the solution to a 100-ml volumetric flask, dilute with water to the mark, mix the solution well, and measure the optical density of the solution against a reference solution containing 12 g of cobalt per litre. Prepare a calibration graph with solutions containing 14–26 g of cobalt per litre. (The calibration solutions can be prepared as described under *Reagents*.) Chromium(III) causes high positive errors.

Zusammenfassung—Kobalt(II)-Ionen können als Perchlorat mit einer spektralphotometrischen Differenzmethode bestimmt werden, wenn die Kobaltproben mit Überchlorsäure bis zum Erscheinen von Überchlorsäurenebeln eingedampft werden. Aus dem Absorptionsspektrum von Kobalt(II)-perchlorat wurde die Bande bei 19,600 cm⁻¹ bzw. 511 m μ zur Bestimmung ausgewählt. Durch systematische Untersuchung der optimalen Konzentrationen ließ sich zeigen, daß die Konzentrationsbestimmung auf besser als 1% genau ausgeführt werden kann, wenn als Vergleichslösung eine Lösung mit 12 g Kobalt pro Liter verwendet wird. Der photometrische Fehler wird dabei kleiner als 0,1%. Der Einfluß einiger Fremdmetalle wurde untersucht; dreiwertiges Chrom gibt hohe Plusfehler. Andere untersuchte Metallionen haben keinen nennenswerten Einfluß.

Résumé—On peut doser les ions cobalt(II) par une méthode spectrophotométrique différentielle, à l'état de perchlorate, après évaporation des échantillons de cobalt avec de l'acide perchlorique, jusqu'à apparition de fumées de cet acide. Dans le spectre d'absorption du perchlorate

de cobalt(II), on a choisi, pour ce dosage, le pic situé à $19,600\text{ cm}^{-1}$ (511 millimicrons). Par l'étude systématique des limites de la concentration optimale, nous pouvons établir que, si l'on emploie une solution contenant 12 grammes de cobalt par litre comme référence, la détermination de la concentration peut être effectuée avec une erreur inférieure à 1%, cependant que l'erreur photométrique correspondante est inférieure à 0,1%. On a étudié l'influence de quelques métaux étrangers. Parmi ceux-ci le chrome, s'il est présent à l'état trivalent, est cause d'erreurs positives élevées. D'autres ions métalliques examinés n'ont pas d'effet significatif.

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THE DETERMINATION OF SODIUM, POTASSIUM, MAGNESIUM, MANGANESE AND CALCIUM IN CEMENT BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY

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Summary—Various aspects of the determination of sodium, potassium, magnesium, manganese and calcium in cement by atomic-absorption spectrophotometry are described. For the determination of sodium, potassium and magnesium, both the calibration curve method and the addition method were found suitable because of the linear relationship between absorption and concentration. For the determination of manganese and calcium, the calibration curve method was found suitable. The calibration curves for sodium and potassium must be prepared to contain the same concentration of calcium as the analysed samples. The method is rapid, and no preliminary separations are necessary. The precision for the determination of sodium, potassium, magnesium and manganese is satisfactory, but is insufficient for calcium because of the large calcium content of cement.

INTRODUCTION

CURRENT methods for determining sodium, potassium, magnesium, manganese and calcium in cement include flame-emission techniques for sodium and potassium, titration with ethylenediaminetetra-acetic acid for magnesium and calcium, and a photometric technique for manganese. The phenomena of self and mutual interferences are observed in the flame-emission methods for alkalis.¹ Magnesium and manganese can also be determined by the flame-emission method. This method, however, is insufficiently sensitive.

The method of atomic-absorption spectrophotometry has been found suitable for use in routine analysis because of the marked freedom from interference, the high degree of accuracy and the simplicity of operation compared with other procedures. The aim of the work described in this paper was to examine the application of atomic-absorption spectrophotometry to the determination of sodium, potassium, magnesium, manganese and calcium in cement.

EXPERIMENTAL

Apparatus

The instrument used in this work was a Hitachi photoelectric spectrophotometer EPU-2, together with the Hitachi atomic-absorption attachment RA-1. Fig. 1 shows the optical system of the equipment. The electrical emission-compensation system was used to measure the intensity of the absorbed radiation without interference by emission from the vaporised sample.

The 7-cm fish tail burner, which could use an air-acetylene mixture, was water-cooled throughout the work. A sample solution was atomised into the spray chamber by an air stream. Acetylene was introduced directly into the burner, and mixed with the air from the spray chamber at the bottom of the burner.

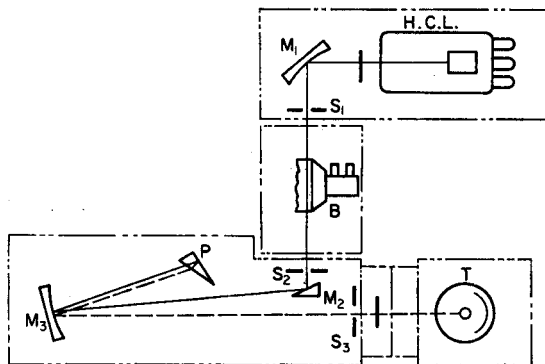


FIG. 1.—Optical system of Hitachi atomic absorption spectrophotometer.

H.C.L.: Vapour discharge lamp or hollow-cathode lamp.

M_1, M_2, M_3 : Mirrors.

S_1, S_2, S_3 : Slits.

P: Prism.

T: Photomultiplier tube.

Operating conditions

The optimum conditions listed in Table I were established by preliminary work with solutions of pure sodium, potassium, magnesium, manganese and calcium.

Lamp current: The lowest possible lamp current was necessary for operating the magnesium or calcium cathode lamps. The magnesium hollow-cathode lamp (Mg-Al cathode) used in this work could not be operated with a current less than 30 mA because of the low light intensity of the lamp and poor sensitivity of the detector for low light intensity. The limit of detection of magnesium in the present method is $1 \mu\text{g/ml}$. The effect of lamp current on magnesium absorption is shown in Fig. 2. However, the manganese lamp showed an increase of sensitivity with increase in lamp current (Table II).

Acetylene pressure: After the air pressure had been set at a constant value (1.4 Kg/cm^2), an examination was made of the effect on absorbance when the acetylene pressure was varied. The position of the passage of the beam from the hollow-cathode lamp through the flame was set at 6 mm above the burner top. The top of the inner cone was 4 mm above the burner top. No incandescence in the flame was observed at 0.32 Kg/cm^2 of acetylene. The top of the inner cone varied and the incandescence increased with increase of the acetylene pressure. The incandescence was visible in the whole of the flame at 0.46 Kg/cm^2 of acetylene. The results are summarised in Fig. 3. From these results it can be seen that an acetylene pressure from 0.32 to 0.46 Kg/cm^2 seems to have no effect on absorbance of sodium, magnesium and manganese. The absorbance of calcium varied,

TABLE I.—OPTIMUM CONDITIONS FOR DETERMINATION OF SODIUM, POTASSIUM, MAGNESIUM, MANGANESE AND CALCIUM

Element	Light source	Lamp current, mA	Lines, Å	Slit width, mm
Na	Sodium lamp (Toshiba)	—	5890	0.03
K	Potassium lamp (Hitachi)	—	7665	0.15
Mg	Hollow-cathode lamp (Mg-Al)*	30	2852	0.03
Mn	Hollow-cathode lamp (Mn-Cu)*	75	2798	0.15
Ca	Hollow-cathode lamp (Ca-Al)*	50	4225	0.035

* Hitachi hollow-cathode lamp.

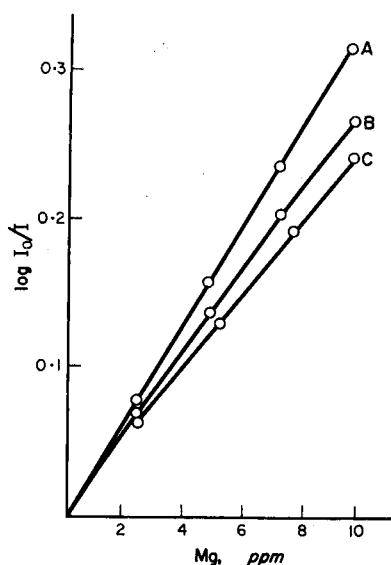


FIG. 2.—Effect of lamp current on magnesium absorption.

A: 30 mA.

B: 40 mA.

C: 50 mA.

and that of potassium varied slightly with variation in the acetylene pressure. The smallness of the region over which calcium atoms in the flame are abundant may be responsible for the variation of the absorbance with the variation of the height of the inner cone.

Slit width: Experiments were made at various slit widths. The slit widths shown in Table I were necessary to obtain satisfactory results. Because of the fluctuation of emission, the small slit width was adequate for compensating the emission from sodium. The increased absorption was obtained for manganese by opening the slit. Too wide a slit may result in unsatisfactory precision.

Relation between absorption and concentration of elements

Calibration curves were prepared for sodium, potassium, magnesium or manganese without calcium and containing calcium. The resulting curves are shown in Fig. 4. In the presence of calcium, depression of the sodium and potassium absorptions was observed. Therefore a calibration curve for the analysis of cement must be prepared by the addition of calcium. Magnesium absorption was not affected by the presence of 500 ppm of calcium. Larger amounts of calcium did affect the magnesium absorption. Sodium, potassium and magnesium can be determined by the addition method, because the curves indicate linearity, within the limits of experimental error, in the presence of calcium. Because slightly curved calibration curves were obtained for manganese and calcium,

TABLE II.—EFFECT OF LAMP CURRENT ON ABSORPTION FROM MANGANESE-COPPER HOLLOW-CATHODE LAMP

Lamp current, mA	Absorbance to manganese ^a
45	0.184
55	0.201
65	0.213
75	0.239
85	0.244
95	0.244

^a 38 ppm.

the addition method was not useful for these elements in cement. The calibration curve for manganese could be prepared in the absence of calcium.

Reproducibility

Reproducibility was determined by repeatedly measuring the absorption of solutions containing sodium, potassium, magnesium, manganese or calcium. The coefficients of variation were 1.3% for a solution containing 5.8 ppm of sodium, 1.1% for a solution containing 23 ppm of potassium,

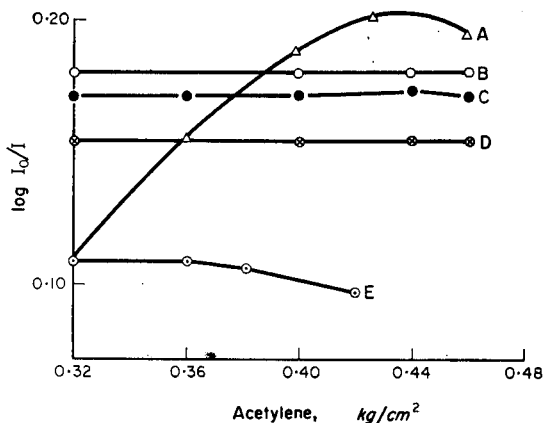


FIG. 3.—Effect of flame condition on the absorption of sodium, potassium, magnesium, manganese and calcium.

- A: Calcium.
- B: Sodium.
- C: Manganese.
- D: Magnesium.
- E: Potassium.

(Air pressure kept constant at 1.4 Kg/cm².)

1.5% for a solution containing 7.4 ppm of magnesium, 2.3% for a solution containing 26 ppm of manganese and 1.2% for a solution containing 101 ppm of calcium.

Interferences

A systematic investigation of interference effects was carried out, using various amounts of other elements. Apart from calcium, other elements, in the proportions normally found in cement, had no effect on the determination of sodium and potassium. The majority of elements did not interfere with the determination of manganese. Serious interference for magnesium in pure solution was observed in the presence of aluminium and silicon (Fig. 5). But these interference effects were not observed in the analysis of cement because of the suppression effect of calcium present in the sample on the aluminium (or silicon) interference. Phosphorus interference was observed in an air-propane flame, but not in an air-acetylene flame. Calcium absorption was interfered with in the presence of aluminium, silicon and phosphorus. The addition of large amounts of strontium was necessary to suppress the interference.

The solutions used for the analysis were about 0.24M in hydrochloric acid, and this was sufficient to give results lower by 20% than for solutions containing no free acid. Sulphuric or perchloric acid behaved in much the same way as hydrochloric acid.

Enhancement of absorption was obtained by the addition of acetic acid, alcohols and acetone to the solution. An increase in sensitivity of about 3-fold by the addition of 50% of propanol or about 5-fold by the addition of 50% of acetone was obtained, similar increases being obtained for the different elements.

Recommended procedure

Decompose 0.5 g of sample with 20 ml of hydrochloric acid (4M), heat and evaporate to dryness. Dissolve the residue in 5 ml of hydrochloric acid (4M) and filter through a filter paper into a 100-ml

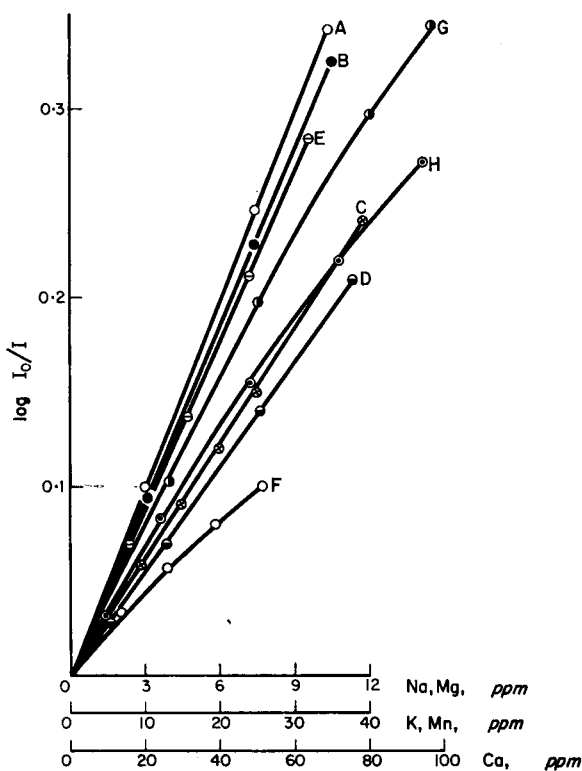


FIG. 4.—Typical calibration curves for sodium, potassium, magnesium, manganese and calcium.

- | | |
|----------------------------------|---|
| A: Na without Ca. | E: Mg without Ca and containing 503 ppm of Ca. |
| B: Na containing 3350 ppm of Ca. | F: Mn without Ca and containing 3350 ppm of Ca. |
| C: K without Ca | G: Ca without Sr. |
| D: K containing 3350 ppm of Ca. | H: Ca containing 5000 ppm of Sr. |

volumetric flask, washing with small volumes of hot water. Cool the filtrate and dilute to the mark with cold water.

Sodium: Take three 10-ml portions of the sample stock solution. Add 25 ml of solutions of sodium chloride containing 6, 12 and 18 ppm of sodium to these, and dilute each solution to 50 ml with water. Spray the solutions into the flame, and measure the absorbance. Plot the absorbance against the added amounts of sodium and read the amount of sodium in the original sample by extrapolating the linear relation curve of absorption *versus* concentration to zero absorbance.

Potassium: Take three 10-ml portions of the sample stock solution. Add 5 ml of solutions of potassium chloride containing 20, 40 and 60 ppm of potassium to these, and dilute each solution to 20 ml with water. Proceed as for sodium.

Magnesium: Take three 5-ml portions of the sample stock solution. Add 25 ml of solutions of magnesium chloride containing 4, 8 and 12 ppm of magnesium to these, and dilute each solution to 50 ml with water. Proceed as for sodium.

Manganese: Spray the sample stock solution into the flame and measure the absorbance. Obtain the manganese content of the sample by reference to a previously prepared calibration curve which was prepared from standard solutions containing the same concentration of acid as the sample solution.

Calcium: Take 5 ml of the sample stock solution. Add 50 ml of a solution of strontium chloride containing 25,000 ppm of strontium, and dilute to 250 ml with water. Proceed as for manganese.

Sodium, potassium and magnesium can also be determined using calibration curves as for manganese or calcium.

partially evaporated and so liberate only a small proportion of the sodium atoms present. The magnitude of the effect of calcium depended on the atomiser. The use of a more efficient atomiser might suppress the effect of calcium. Rubeška *et al.*⁴ have also discussed the effect of calcium on the sodium absorption.

Elwell and Gidley⁵ described the marked effect of silicon on magnesium absorption using an air-coal gas flame. The present authors found no interference from silicon using an air-acetylene flame.

The addition method was found to be satisfactory for the analysis of cement for sodium, potassium and magnesium, because of the linear relationship between absorption and concentration. Results obtained by both addition and calibration curve methods, in the determination of sodium and magnesium in cement, are in good agreement; but results for potassium by the addition method are lower by 10% than those by the calibration curve method.

It was found, in agreement with David,⁶ that interference from aluminium, silicon and phosphorus, in the determination of calcium, was suppressed by the addition of large amounts of strontium. The results for calcium would, however, be lacking in precision because of the large calcium content of cement.

Zusammenfassung—Verschiedene Gesichtspunkte bei der Bestimmung von Natrium, Kalium, Magnesium, Mangan und Calcium in Zement durch atomare Absorptionsspektralanalyse werden untersucht. Bei der Bestimmung von Natrium, Kalium und Magnesium wurden sowohl die Eichkurvenmethode als auch die Additionsmethode für geeignet befunden, da Absorption und Konzentration linear zusammenhängen. Zur Bestimmung von Mangan und Calcium ist die Eichkurvenmethode geeignet. Die Eichkurven für Natrium und Kalium mußten in Gegenwart der selben Calciumkonzentration wie in der Probe aufgenommen werden. Die Methode geht schnell und bedarf keiner vorausgehenden Trennung. Die Genauigkeit der Bestimmung von Natrium, Kalium, Magnesium und Mangan ist befriedigend, bei Calcium ist sie wegen des hohen Calciumgehaltes von Zement unzureichend.

Résumé—On décrit l'étude de divers aspects du dosage de sodium, potassium, magnésium, manganèse et calcium dans le ciment, au moyen de la spectrophotométrie d'absorption atomique. Pour le dosage de sodium, potassium et magnésium, les méthodes par courbe d'étalonnage et par addition sont toutes deux convenables, par suite de la relation linéaire entre l'absorption et la concentration. Pour le dosage de manganèse et calcium, la méthode par courbe d'étalonnage est convenable. Les courbes d'étalonnage pour le sodium et le potassium doivent être préparées en présence d'une concentration en calcium égale à celle des échantillons analysés. La méthode est rapide, et ne nécessite pas de séparations préliminaires. La précision est satisfaisante pour le dosage de sodium, potassium, magnésium et manganèse, mais elle est insuffisante pour le calcium par suite de la forte teneur du ciment en cet élément.

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CHELATING PROPERTIES OF THE CHELATING ION EXCHANGER DOWEX A-1*

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Summary—The properties and behaviour of the chelating ion exchanger Dowex A-1 have been studied when in contact with an aqueous solution containing metal ions complexed with aminocarboxylic ligands. The stability constants of the metal ion complexes with the resin have been determined as well as the structure of the complexes formed by the metal ions, the resin and the ligands in the solution. Dowex A-1 behaves as a solid complexing agent and forms stable 1:1 complexes with metal ions.

FUNDAMENTAL research carried out so far on Dowex A-1, a chelating ion exchanger, has dealt mainly with kinetics^{1,2,3}, equilibrium studies,⁴ separation possibilities,⁵ and the effects of the medium.⁶

In the present work an attempt is made to solve problems of a new kind, connected with the mechanism of binding metal ions to this resin and with the stability of the complexes formed. This raises a number of secondary problems, such as the structure of the resin, the ligands entering together with the metal ions, the definition of the order of affinity of the metals, the connection between the stability of the metal complexes in solution and their adsorbability, *etc.* Answers to these fundamental questions should further applied analytical research on Dowex A-1 and contribute towards an understanding of complexation mechanisms in general.

It is proposed to show how information on the structure of the complexes and their stability may be obtained with the help of simple equilibrium experiments in a solid-liquid system (the solid being Dowex A-1, the liquid being metal ions in aqueous solution bound to aminocarboxylic ligands) where chelation takes place in both phases, which are easily separable and analysable after equilibrium has been attained.

DISCUSSION

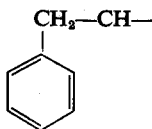
Structural considerations

Much information regarding the structure of Dowex A-1 is obtainable from elemental analysis of the sodium form of the resin. The composition of a homogeneous sample specimen of the sodium resin, when dried at 100°, is as follows:

C—	52.91%
H—	6.26%
N—	3.50%
O—	25.63%
Na—	11.7%.

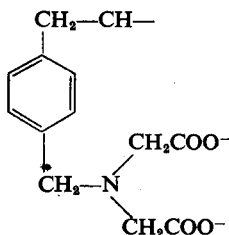
Dowex A-1 is a polymer composed of styrene-divinylbenzene rings, some of which are substituted by iminodiacetic acid (IDAA).

(a) *Calculation of number of substituted rings.* Assume that the resin is composed of two kinds of rings : A-rings, aromatic rings which have no functional group,



C_6H_6 (molecular weight 104)

and B-rings, aromatic rings substituted by IDAA.



$C_{13}H_{13}NO_4$ (molecular weight 247)

Because nitrogen is present only in the substituted rings, the number of B-rings may be calculated on the strength of the nitrogen content. The content of 3.5% of nitrogen means that each 1 g of resin contains 2.5 mmole of nitrogen or 2.5 mmole of B-rings.

One g of resin, therefore, contains 617 mg of B-rings ($2.5 \times 247 = 617$ mg), but the balance does not give the number of A-rings, because in the substance dried at 100° water molecules are still bound as ligands to the metal ion. The required data will, however, be provided by the material balance of carbon atoms.

(b) *Carbon balance.* The carbon content being 52.91%, 1 g of resin contains 44 mmole of carbon, of which the B-rings have taken up $2.5 \times 13 = 32.5$ mmole of carbon. The balance ($44 - 32.5 = 11.5$ mmole of carbon) is available for A-rings. From this it may be inferred that of every 8 rings there are 5 substituted ones,* *i.e.*, not all rings are substituted. The chelating ligands in the resin are, therefore, well spaced, so that a metal ion is unlikely to be bound to two IDAA ligands from the resin.

(c) *Calculation of water content.*

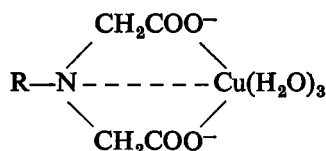
One g of resin contains	2.5 B-rings = 617 mg
	1.45 A-rings = 150.8 mg
	11.7% of Na = <u>117 mg</u>
	<u>884.8 mg</u>

* The basis of this inference is as follows. B-rings contain 13 carbon atoms, so that the amount taken up by them is $13 \times 2.5 = 32.5$ mmole of carbon. In the A-rings, on the other hand, there are only 8 carbon atoms and, because only $44 - 32.5 = 11.5$ mmole are left, there can only be $11.5/8 = 1.45$ A-rings. From this it is concluded that for every 8 rings in the resin there are 5 substituted ones.

giving a balance of 115 mg of water. The fact that water remains in the resin and does not evaporate at 100° is interesting in itself, because it proves the penetration of the ligands, together with the metal ions, from the solution into the resin matrix.

(d) *Oxygen balance.* Subtracting the proportion bound to water (10.2%) from the over-all percentage of oxygen (25.63%), for each mmole of nitrogen there are 4 mmole of oxygen, which corresponds to the structural considerations of the rings substituted by IDAA.

(e) *Structure of resin when containing copper.* Elemental analysis of the copper-containing resin produces results similar to the sodium-containing resin, so far as carbon, nitrogen, oxygen and hydrogen contents are concerned. The water balance shows that for each mmole of copper in the resin 3 molecules of water enter. This gives rise to the assumption that the structure of the complex formed by copper and Dowex A-1 is as follows



where R is the polymer matrix. Copper is thus seen to enter the resin in an octahedral configuration,¹⁵ and it will be shown later that if the copper in the solution is bound to chelating ligands, it will also enter the resin with these ligands instead of with water.

Stoichiometry

In order to understand the stoichiometry of the reactions between the metal ions and Dowex A-1, measurements of the maximum capacity of the resin may be used. Experimentally, this is done by bringing a known weight of dry resin in contact with solutions of increasing concentration of the metal ion. Experiments were conducted with Cu²⁺, Pb²⁺, Fe³⁺ and Th⁴⁺ ions, and in all cases similar results were obtained, viz., 2.4–2.5 mmole of metal ions/g of Dowex A-1. Because 1 g of resin contains 2.5 mmole of IDAA, it is found that metal ions are complexed by the resin in the stoichiometric ratio of 1:1, independent of valency. This is similar to the stoichiometry of the reactions of EDTA with metal ions in solution.

A marked difference in behaviour is seen to exist between IDAA in solution and in the resin matrix. In solution the metal ions combine with more than 1 molecule of IDAA, in accordance with their valency, while in the resin complexation is accomplished in a single step, from which it may be concluded that the complexes in the resin are more stable than those formed in solution.

Metal and ligand sorption

In a system consisting of a certain quantity of dry resin in contact with a solution containing a few mmole of metal ions bound to an excess of a tridentate ligand, such as IDAA, the relation between the concentration of ligands in solution and the resin's adsorptive capacity for metal ions must be established. Obviously, increasing the concentration of the ligand in the solution reduces the concentration of ions in

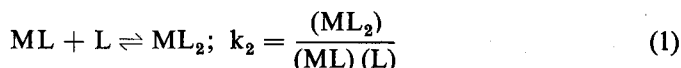
the resin because of competing complexation. Experiments have shown two important facts:

(a) A definite quantitative relation exists between the stability constants of the metal ion complexes with the ligands in solution and their adsorbability on the resin.

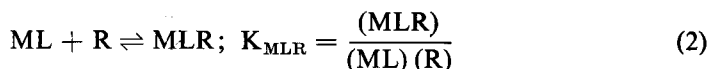
(b) Stoichiometric penetration takes place of 1 IDAA molecule together with 1 metal ion.

The significant equilibria involved in this experimental system are as follows

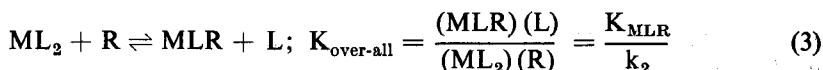
In Solution



In Resin Phase



Over-all Reaction



or expressed logarithmically

$$\log(L) = \log \frac{(ML_2)(R)}{(MLR)} + \log K_{\text{over-all}} \quad (3a)$$

where L represents the polydentate ligand and R represents the polymer matrix.

The quantities appearing in equation (3a) are defined as follows:

(MLR) = The quantity of metal present in the resin after the system has reached equilibrium.

(L) = The quantity of uncomplexed ligand (the quantity of ligand introduced minus the quantity of ligand bound to the metal).

(ML₂) = The quantity of metal complex remaining in solution after phase separation; this may be calculated by subtracting the quantity of metal bound to the resin from the total quantity of metal introduced into the system.

(R) = The quantity of resin not bound to the complexing metal ion; this may be calculated by subtracting the quantity of (MLR) from the maximum capacity of the resin.

The quantities in the brackets denote the concentrations of the various species. The concentrations of the constituents in the solution (ML₂, ML and L) are expressed in mmole/100 ml, while those in the solid phase are in mmole of metal ions (which is equivalent to the number of mmole of chelating groups in the resin) (cf. Table I). K_{over-all} is an apparent constant. It is the quotient of the stability of the mixed complex in the resin phase divided by the stability of the complex in the solution. If the proposed mechanism is correct, the graphic correlation of log(L) vs. log [(ML₂)(R)]/(MLR) should be a straight line of unit slope, the intersection of which with the x-axis gives K_{over-all}; k₂ may be found from the literature, hence K_{MLR}.

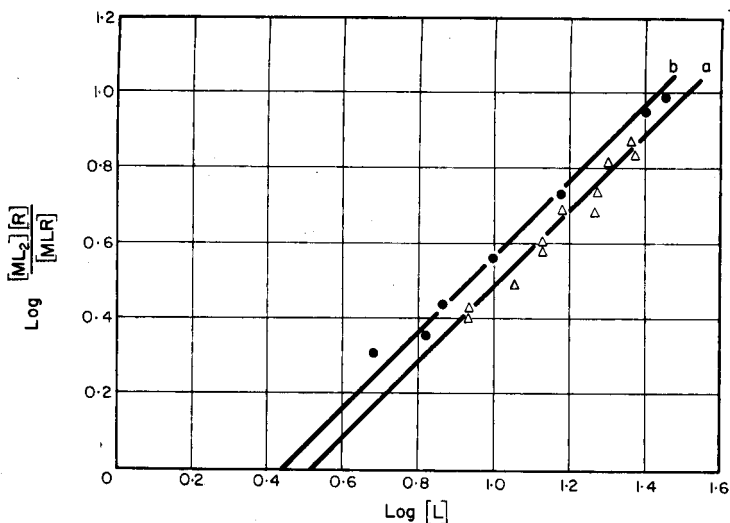


FIG. 1.—Graphical correlations from equilibrium measurements of:
 (a) Cu^{2+} with IDAA in contact with 0.5-g portions of Dowex A-1.
 (b) Ni^{2+} with IDAA in contact with 0.5-g portions of Dowex A-1.

may be determined. Fig. 1 shows that the results of the experiments with copper and nickel bound to IDAA confirm the above theoretical considerations.

Similar experiments were made by binding the copper ion to other ligands, such as glycine and glutamic acid. Here too, straight lines were obtained with a slope close to unity (Fig. 2). The slight deviations from unit slope are probably from neglecting the activity coefficients.

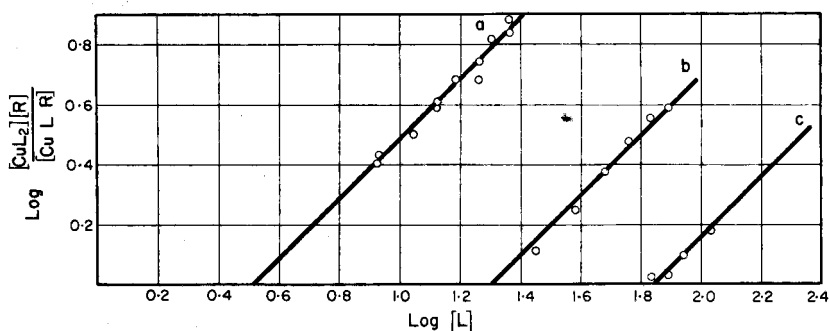
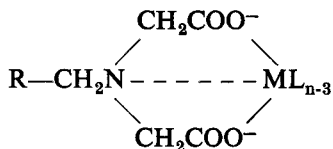


FIG. 2.—Equilibrium measurements of copper ions with various aminocarboxylic acid ligands [equation (3a)]:
 (a) IDAA,
 (b) glutamic acid,
 (c) glycine.

Ligand sorption in cation exchangers was first described by Stokes and Walton⁷ and its theory elaborated by Helfferich,^{8,9} who made use of the phenomenon for ligand exchange and separations in columns containing metal ions bound to ion exchangers.

It can now be definitely concluded that the structure of the complex formed is



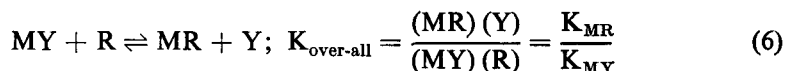
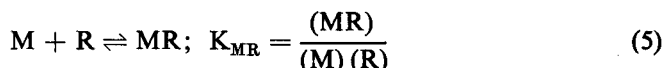
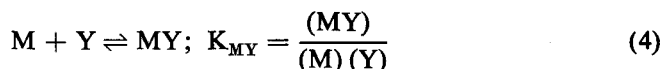
L denotes the additional ligand to which the metal is bound in the resin phase. It may consist of water molecules, an anion of the salt of the metal in the solution or an aminocarboxylic ligand, as was shown before. n is the co-ordination number of the metal.

Determination of stability constants of metal ions with Dowex A-1

So far the formation of mixed complexes consisting of metal ions, Dowex A-1 and bi- or tridentate ligands has been discussed. Now the order of affinity of the metals to the resin must be established.

When an aqueous solution containing several metal ions is passed through a column of Dowex A-1, the ions will enter the resin according to a certain order, which depends on the stability constants of the metals with the resin. In order to determine a constant of the type K_{MR} , the resin must be brought into contact with a solution containing metal ions bound to a large polydentate ligand, such as EDTA or the like, which, because of its bulky molecules and the stereospecificity of its complexes, will not enter the resin, as did IDAA or glycine. The result will be that the hydrated metal ion alone will enter the resin.

In this system two competing complexation reactions take place



$$\log(R) = \log \frac{(MR)(Y)}{(MY)} - \log K_{\text{over-all}} \quad (6a)$$

Y denotes the large polydentate ligand to which the metal ion in the solution is bound. In the present case the ligand selected was *N*-hydroxyethylenediaminetriacetic acid (HEDTA). R again denotes the polymer matrix.

Analogously to K_{MLR} , K_{MR} may be found by graphic correlation of $\log(R)$ vs. $\log [(MR)(Y)/(MY)]$. In Fig. 3 the constants for nickel and copper within the resin are determined experimentally. For these equilibrium measurements HEDTA was chosen because it binds these metal ions more strongly than Dowex A-1 ($\log K_{NiY} = 17.0$; $\log K_{CuY} = 17.4$) and gives convenient distribution ratios of the ions between the resin and the solution. The lines obtained in Fig. 3 are straight

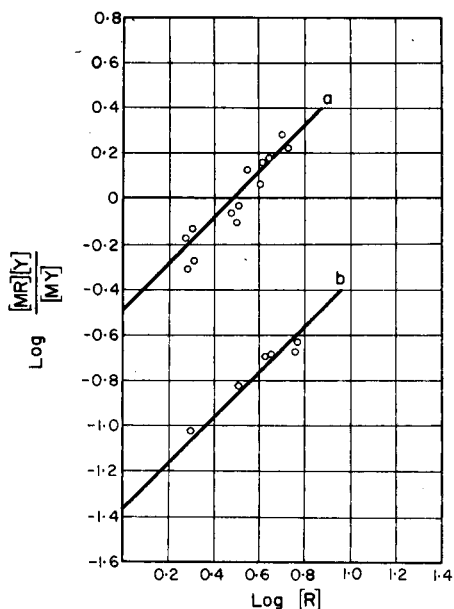


FIG. 3.—Graphical determination of stability constants [equation (6a)] of:

- (a) Cu^{2+} with Dowex A-1,
 (b) Ni^{2+} with Dowex A-1.

and of unit slope, which proves the correctness of the proposed mechanism [equations (4) and (5)] and also the fact that a ligand of the type HEDTA does not enter the resin. A further conclusion to be drawn is that Dowex A-1 behaves similarly to the complexation agents in the solution, and that its property to bind the metals to the solid phase makes it a convenient and effective means for the study of complexation mechanisms.

EXPERIMENTAL

Reagents

0.1M Standard copper solution: Prepared by dissolving 7.594 g of reagent-grade copper^{II} oxide in nitric acid (1:1), evaporating excess acid and making up to 1 litre.

0.1M Standard nickel nitrate solution: Prepared by dissolving 29.08 g of reagent grade $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in distilled water and making up to 1 litre.

0.1M Standard EDTA solution: Prepared by dissolving 37.21 g of pure disodium dihydrogen ethylenediaminetetra-acetate dihydrate in distilled water and making up to 1 litre.

Complexing agents

Dowex A-1 chelating resin was prepared in the sodium form from the Dow Chemical Co. product and dried at 100°. Glycine, monosodium glutamate, iminodiacetic acid (IDAA) and *N*-hydroxy-ethylenediaminetriacetic acid (HEDTA) were used as analytical-grade solids.

Procedure for distribution measurements of cations from solutions containing complexing ligands (Figs. 1 and 2)

Weighed portions of the dried sodium form of the resin (exactly 500 mg) were placed into 250-ml beakers. To each beaker were added 100 ml of solution containing 1 mmole of copper or nickel ion and varying quantities of the complexing ligands (5–40 mmole). The pH of all solutions was adjusted to 8.5 to diminish the "pH effect" (the effect of the hydrogen ions on the stability of the complexes). The solutions were magnetically stirred for 2 hr in a water bath of 70° and for a further 2 hr at room temperature. Experience has shown that heating considerably speeds up the reaction. Without heating, equilibrium is reached after not less than 17–18 hr. After equilibrium the phases were separated at room temperature (23–27°) by means of filtration and the metal ions eluted from the resin with 6M nitric acid. Copper was determined polarographically with EDTA,⁶ and nickel gravimetrically with dimethylglyoxime.

Knowing the general quantity of metal ions and ligand introduced into the system and the quantity of the metal ions adsorbed by the resin, all of the other quantities required for the construction of Figs. 1 and 2 may be calculated.

Procedure for determination of stability constants

The experimental set-up is identical with that described in the previous paragraph, with the exception that because $\log(R)$ appears in the abscissa of Fig. 3, different quantities of resin had to be weighed. Table I shows the concentrations of the different components with which the required data for line (a) of Fig. 3 were obtained.

TABLE I.—EQUILIBRIUM MEASUREMENTS FOR THE COPPER-HEDTA SYSTEM

No.	Cu ²⁺ taken, mmole ₃ 100 ml	HEDTA taken, mmole ₃ 100 ml	Resin ₃ g	pH	Cu ²⁺ found in resin phase (Cu R), mmole	Uncomplexed HEDTA left in solution (Y), mmole	Cu-HEDTA found in solution (MY), mmole	Resin ^a left uncomplexed (R), mmole
1	0.500	1.000	1.000	10.6	0.250	0.750	0.250	2.150
2	0.500	1.000	1.250	10.7	0.265	0.765	0.235	2.735
3	1.000	1.000	1.500	10.3	0.591	0.591	0.409	3.009
4	1.000	1.000	2.000	10.2	0.678	0.678	0.322	4.122
5	1.000	2.000	1.000	10.3	0.334	1.334	0.666	2.066
6	1.000	2.000	2.000	10.6	0.500	1.500	0.500	4.300
7	1.000	2.000	2.500	10.2	0.600	1.600	0.400	5.400
8	1.500	3.000	1.500	10.1	0.452	1.952	1.048	3.148
9	1.500	3.000	2.000	9.9	0.543	2.043	0.957	4.257
10	1.500	3.000	2.500	10.0	0.641	2.141	0.859	5.359
11	1.500	3.500	1.000	10.1	0.292	2.292	1.208	2.108
12	1.500	3.500	1.500	10.0	0.408	2.408	1.092	3.192

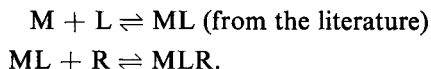
^a Calculated by subtracting (CuR) from the maximum capacity of the resin (2.4 mmole/g).

RESULTS

Table II summarises the numerical results obtained for the stability constants of the mixed metal-ligand-resin complexes and of the hydrated nickel and copper ions with Dowex A-1. For comparison, stability constants of these metals with the same ligands (IDAA, glycine, glutamic acid and HEDTA) in aqueous solutions, taken from the literature, are also quoted.

The constants for reactions of the type $ML + R \rightleftharpoons MLR$ were calculated from the intercepts with the x-axis in Figs. 1 and 2, utilising equation (3a).

The constants for reactions of the type $M + L + R \rightleftharpoons MLR$ were taken as the sum of two reactions



The constants for reactions of the type $M + R \rightleftharpoons MR$ were calculated from the intercepts with the y-axis in Fig. 3.

From the numerical results shown in Table II two important conclusions may be drawn:

(1) The stability constants of mixed complexes of the type MLR are higher than the sum of the stepwise complexation constants of the metals with the ligands in the solution. This was also proved for the mixed complexes in aqueous solution of the metal chelonates with ammonia and the hydroxyl and hydrogen ions, the stability of which is greater than that of the pure metal chelonates.¹⁴

(2) The stability constants of complexes of the type MR are lower than those of the corresponding metals with HEDTA, but higher than the sum of the stability

TABLE II.—STABILITY CONSTANTS OF COPPER AND NICKEL WITH SOME AMINOCARBOXYLIC LIGANDS

Reaction investigated	Stability constant (log K)	Reference
${}^a\text{Cu} + \text{IDAA} \rightleftharpoons \text{Cu}-\text{IDAA}$	10.55	10
${}^a\text{Cu} - \text{IDAA} + \text{IDAA} \rightleftharpoons \text{Cu}(\text{IDAA})_2$	5.65	10
$\text{Cu} - \text{IDAA} + \text{R} \rightleftharpoons \text{Cu}(\text{IDAA})\text{R}$	6.17	
$\text{Cu} + \text{IDAA} + \text{R} \rightleftharpoons \text{Cu}(\text{IDAA})\text{R}$	16.72	
${}^a\text{Cu} + \text{Glycine} \rightleftharpoons \text{Cu}-\text{Glycine}$	8.38	11
${}^a\text{Cu} - \text{Glycine} + \text{Glycine} \rightleftharpoons \text{Cu}(\text{Glycine})_2$	6.87	11
$\text{Cu} - \text{Glycine} + \text{R} \rightleftharpoons \text{Cu}(\text{Glycine})\text{R}$	8.72	
$\text{Cu} + \text{Glycine} + \text{R} \rightleftharpoons \text{Cu}(\text{Glycine})\text{R}$	17.10	
${}^a\text{Cu} + \text{Glutamate} \rightleftharpoons \text{Cu}-(\text{Glutamate})$	7.85	12
${}^a\text{Cu} - \text{Glutamate} + \text{Glutamate} \rightleftharpoons \text{Cu}(\text{Glutamate})_2$	6.45	12
$\text{Cu} - \text{Glutamate} + \text{R} \rightleftharpoons \text{Cu}(\text{Glutamate})\text{R}$	7.76	
$\text{Cu} + \text{Glutamate} + \text{R} \rightleftharpoons \text{Cu}(\text{Glutamate})\text{R}$	15.61	
${}^a\text{Ni} + \text{IDAA} \rightleftharpoons \text{Ni}-\text{IDAA}$	8.21	10
${}^a\text{Ni} - \text{IDAA} + \text{IDAA} \rightleftharpoons \text{Ni}(\text{IDAA})_2$	6.35	10
$\text{Ni} - \text{IDAA} + \text{R} \rightleftharpoons \text{Ni}(\text{IDAA})\text{R}$	6.79	
$\text{Ni} + \text{IDAA} + \text{R} \rightleftharpoons \text{Ni}(\text{IDAA})\text{R}$	15.00	
${}^a\text{Cu} + \text{HEDTA} \rightleftharpoons \text{Cu}-\text{HEDTA}$	17.4	13
$\text{Cu} + \text{R} \rightleftharpoons \text{Cu}-\text{R}$	16.9	
${}^a\text{Ni} + \text{HEDTA} \rightleftharpoons \text{Ni}-\text{HEDTA}$	17.0	13
$\text{Ni} + \text{R} \rightleftharpoons \text{Ni}-\text{R}$	15.61	

^a Numerical data taken from the literature.

constants of the metals with IDAA in aqueous solution. The reason for this is that in an aqueous solution binding to IDAA is accomplished in two steps, but in the resin in one step only.

CONCLUSION

In this work an attempt has been made to extend the general knowledge of chelating ion exchangers as regards their structure and to obtain information on the stability of the complexes formed between two transition metals and Dowex-A1. A connection has been shown to exist between complexation in solution and the adsorbability of the metal ions on the resin. The adsorption of ligands on the resin has been proved quantitatively.

The experimental results obtained in this work may be obtained by other experimental set-ups. Because the ligands used are of high molecular weight, data on ligand sorption may be inferred from measuring the increase in weight of the resin after adsorption. Another possibility is to use ligands labelled with carbon-14 and to measure their activity in the resin. Some tentative experiments were made in these two directions, but the method of graphic correlations appeared to be both the most accurate and the simplest.

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Zusammenfassung—Eigenschaften und Verhalten des chelatbildenden Ionenaustauschers Dowex A-1 wurden im Kontakt mit einer wässrigen Lösung untersucht, die komplex an Aminocarbonsäuren gebundene Metallionen enthielt. Die Stabilitätskonstanten der Metallkomplexe des Harzes wurden bestimmt sowie die Struktur der Komplexe aus Metallionen, Harz und Liganden. Dowex A-1 verhält sich wie ein fester Komplexbildner und gibt mit Metallionen stabile 1:1-Komplexe.

Résumé—On a étudié les propriétés et le comportement de l'échangeur d'ions chélatant Dowex A-1, lorsqu'il est en contact avec une solution aqueuse contenant des ions métalliques fixés par coordination à des groupes aminocarboxyliques. On a déterminé les constantes de stabilité des complexes que donnent les ions métalliques avec la résine, ainsi que la structure des complexes formés par les ions métalliques, la résine et les agents coordinants dans la solution. La Dowex A-1 se comporte comme un agent complexant solide, et forme des complexes stables 1:1 avec les ions métalliques.

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A STUDY OF THE OXIDATION OF MANGANESE(II) AND CHROMIUM(III) IONS BY SILVER(II) OXIDE

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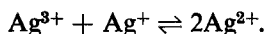
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Summary—A study has been made of the oxidation of manganese(II) and chromium(III) solutions by silver(II) oxide in perchloric acid medium. Both the efficiency and the rate of the oxidation process were found to vary with the concentration of reductant, the amount of AgO added, the temperature, the acidity and the concentration of univalent silver ions in the solution. The inefficiency of the oxidation process can be attributed to the simultaneous formation of oxygen. The results are discussed in terms of a possible reaction mechanism, and the optimum conditions for oxidations using AgO are indicated.

INTRODUCTION

Most titrimetric methods for the determination of manganese and chromium recommend pre-oxidation of these elements by ammonium persulphate in the presence of silver(I) ion as catalyst. The nature of the silver intermediate in these oxidations is not yet established. There is evidence to support both a bivalent and a trivalent species¹ and it has been suggested that the two higher valency silver species may be related through the equilibrium:



The silver(II) ion in solution is a powerful oxidising agent and in the cold almost instantaneously oxidises manganous salts to permanganate² and chromic salts to chromate.³ The bivalent silver ion is also reduced by water, yielding oxygen and silver(I) ion. The rate of reduction by water has been found to be dependent on the concentration and nature of the acid present.^{4,5} Dissolution of silver(II) oxide in acids yields bivalent silver ions.⁶

The use of silver(II) oxide as an oxidimetric reagent for the determination of manganese, cerium and chromium has been examined by Lingane and Davis.⁷ Procedures based on this reagent were found to be faster and more convenient than the classical procedures, and excellent results were obtained in determinations of manganese and chromium in aluminium and iron(II) alloys. Before this study, AgO had been used in microanalysis by Kimira and Murakim⁸ for the determination of manganese and cerium, and by Tanaka^{9,10} for the determination of chromium, manganese and vanadium.

These applications indicate the probable value of silver(II) oxide as an analytical reagent, but more fundamental information on oxidations by this reagent is required. This paper describes the results obtained in a study of the oxidation by silver(II) oxide of manganese(II) and chromium(III) salts in perchloric acid solution. Perchloric acid was chosen as the solvent medium to avoid complications, such as the tendency of chromium salts to form sulphato complexes in sulphuric acid solutions, and the tendency of argentic silver to form nitrate complexes in nitric acid solutions.⁴

EXPERIMENTAL

Reagents

The silver(II) oxide used was prepared according to the directions of Hammer and Kleinberg.¹¹

Standard manganese(II) solutions were prepared from May and Baker R-grade manganese sulphate. The solutions were standardised by oxidation to permanganate with potassium periodate, followed by spectrophotometric measurement of colour intensity.

Chromium(III) perchlorate solutions were prepared by dissolving freshly precipitated hydrated chromium(III) oxide in dilute perchloric acid solutions. The solutions were standardised colorimetrically after oxidation of the chromium by ammonium persulphate using silver ion catalyst. The excess acid present was determined by titration against standard borax solution.

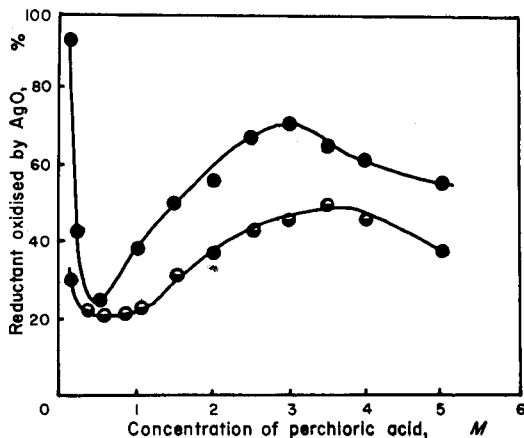


FIG. 1.—The effect of acidity on the amount of metal ion oxidised.

- 0.55 mg of Mn²⁺ treated with 0.021 g of AgO.
- 0.70 mg of Cr³⁺ treated with 0.032 g of AgO.

Perchloric acid solutions of differing concentrations were prepared by dilution of May and Baker 61% and 72% R-grade perchloric acid. The solutions were standardised against standard borax solution.

Apparatus

The apparatus used in the investigation was a water-jacketed reaction cell, fitted with a drain tap, and stirred by a magnetic stirrer. During the studies water was circulated around the cell from a constant temperature tank.

A Coleman Model 14 Spectrophotometer and a Unicam SP 500 Spectrophotometer were used for colorimetric measurements.

Procedure

For equilibrium studies, reaction mixtures were prepared containing varying amounts of reducing agent (0.004–0.050 mg/ml for manganese and 0.0075–0.048 mg/ml for chromium) and varying amounts of acid (0.1–5.5M).

Aliquots (25 ml) of these reaction mixtures were added to the thermostatted reaction cell and stirred to reach thermal equilibrium. Varying amounts of AgO (0.004–0.085 g for manganese and 0.007–0.145 g for chromium) were weighed into small plastic boats. These boats were placed on the surface of the solutions and were subsequently submerged by the stirring action. When the AgO had completely dissolved, the resulting solutions were run off into a receiving vessel and the intensity of colour was measured with a spectrophotometer. The intensity of the permanganate ion was measured at 545 m μ in the Coleman instrument and the dichromate ion was measured at 390 m μ using the Unicam SP 500 instrument. The concentrations of the oxidised products were determined from appropriate calibration graphs. The results of these studies are summarised in Figs. 1 and 2.

Varying amounts of silver(I) ion were added to a series of solutions containing a fixed amount of manganese(II) or chromium(III) salts in solutions 3.0–3.5M in respect of perchloric acid. The results obtained on adding a constant amount of AgO are summarised in Fig. 3.

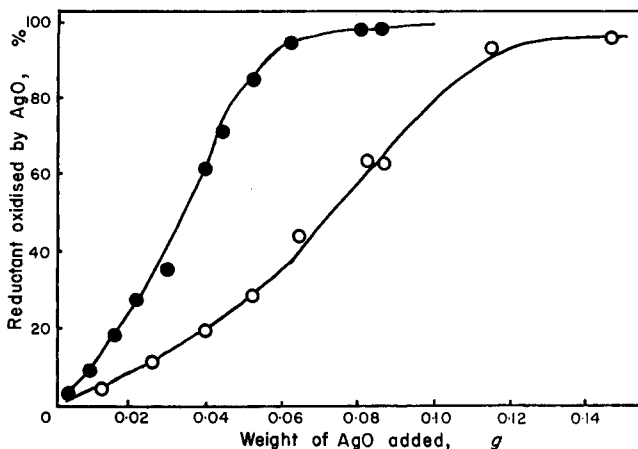


FIG. 2.—The effect of varying weights of silver(II) oxide on the percentage of metal salt oxidised.

- 0.85 mg of Mn²⁺ in 50 ml of 3.5M HClO₄; *t* = 25°; theoretical weight of AgO required for complete oxidation 0.010 g.
- 1.0 mg of Cr³⁺ in 50 ml of 3.0M HClO₄; *t* = 20°; theoretical weight of AgO required for complete oxidation 0.007 g.

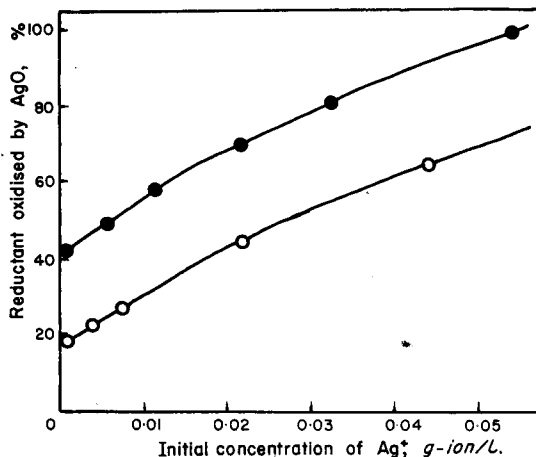


FIG. 3.—The effect of adding silver(I) ion on the percentage of metal salt oxidised.

- 0.5 mg of Mn²⁺ in 25 ml of 1M HClO₄ + 0.022 g of AgO; *t* = 25°.
- 0.7 mg of Cr³⁺ in 25 ml of 1M HClO₄ + 0.037 g of AgO; *t* = 20°.

Finally, oxidations were carried out at different temperatures and the effect of temperature is shown in Fig. 4.

Some studies of the rate of oxidation of the chromium salt at 5° were made, using solutions having acidities varying in concentration from 0.2M to 1.0M. A weighed amount of AgO was added to the solutions in the reaction cell and a sample was extracted from the cell after varying periods of time by means of a pipette fitted with a cotton wool plug to trap particles of unreacted solid. The absorbance of each sample extracted was measured at the appropriate wavelength, and the amount of metal ion oxidised was determined from the calibration graph. These kinetic results were recorded and subsequently treated as a pseudo first order reaction in order to yield the values of apparent rate constants listed in Table I.

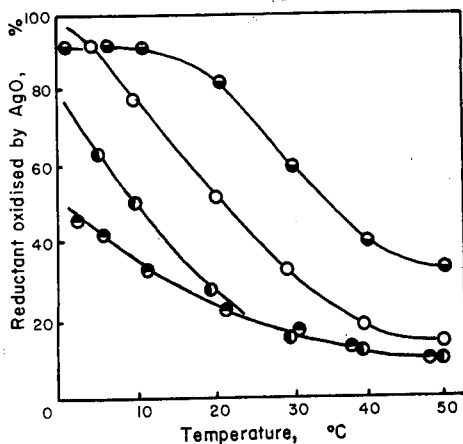


FIG. 4.—The effect of temperature on the percentage of metal salt oxidised.

- 0.5 mg of Mn²⁺ in 25 ml of 3.5M HClO₄ + 0.015 g of AgO.
- ◐—0.5 mg of Mn²⁺ in 25 ml of 3.5M HClO₄ + 0.037 g of AgO.
- ◑—0.7 mg of Cr³⁺ in 25 ml of 3.0M HClO₄ + 0.022 g of AgO.
- 0.7 mg of Cr³⁺ in 25 ml of 3.0M HClO₄ + 0.030 g of AgO.

TABLE I.—RATE OF FORMATION OF CHROMATE ION
(Temperature, 5°)

AgO added, g	Concentration of Cr ³⁺ , g ion/litre × 10 ⁴	Concentration of HClO ₄ , M	Apparent rate constant, k × 10 ³	Initial rate, k _i × 10 ³ mg/sec
0.060	5.44	0.209	2.26	4.38
0.060	5.44	0.413	7.27	8.31
0.060	5.44	1.047	24.0	44.8
0.060	5.44	1.516	33.2	72.4
0.060	2.63	0.40	7.72	7.03
0.060	7.93	0.40	5.90	8.42
0.060	10.6	0.40	7.52	10.9
0.045	5.44	0.40	8.13	7.29
0.090	5.44	0.40	4.54	11.1
0.110	5.44	0.40	4.29	14.5

RESULTS

Although, stoichiometrically, sufficient AgO was added to each solution to oxidise completely all the manganese or chromium present, complete oxidation of these species was only achieved in the presence of a large excess of reagent. To emphasise the effect, the results have been recorded in the form of percentage of the original manganese or chromium ion oxidised to permanganate or chromate.

The effect of acid concentration on the percentage conversion is shown in Fig. 1. Similar curves, displaced vertically, were obtained on adding different weights of AgO. Maximum conversion was obtained with solutions which were either 0.1–0.2M or 3.0–3.5M in respect of perchloric acid. In the former case, the rate of solution of solid was slow (5–15 min) as compared with seconds for the more concentrated solutions.

The effect of adding varying weights of AgO to a given solution is indicated by

the typical results shown in Fig. 2. Total conversion was obtained if sufficient excess of oxidant was added. An interesting side effect was observed in manganese studies using sulphuric acid of equivalent strength. Where the Mn^{2+} was not fully oxidised to permanganate, there was a gradual fading of the initial purple colour, and the formation of a brown precipitate of MnO_2 , indicating that the remaining Mn^{2+} in the presence of Ag^+ was reducing the oxidised species. This effect was not so marked using perchloric acid solutions.

For a given set of conditions, the percentage conversion was considerably increased by the addition of silver nitrate before oxidation, as shown by the results recorded in Fig. 3. The effect of an increase in temperature was to reduce the amount oxidised, as illustrated in Fig. 4.

In the kinetic studies, the oxidation of the chromium(III) ion approximated to a pseudo first order reaction if the ultimate amount of chromate formed was taken to represent the initial concentration of some species responsible for the formation of the chromate. On this basis, values for apparent rate constants under different conditions were calculated for comparison purposes, and these results are summarised in Table I. Initial rates of chromate formation for the varying conditions were estimated from the rate curves and these rates are shown in Table I also. The kinetic values are considered to be of limited accuracy, for it was necessary to separate the solid phase from the solution during collection of the sample, and because the time for complete reaction was only a matter of minutes, slight variations in the rate of sample collection through the filter introduced significant errors.

To obtain mathematical relationships between the results recorded in Table I, the varying sets of results were plotted against each other on log-log paper. In each case a linear relationship was obtained, and the slopes were measured to give the power dependence of the rate on the various factors. Combination of the results yielded the following expressions:

$$\text{Apparent rate constant } k = k_1 \cdot [H^+]^{1.36} \cdot \{AgO\}^{-0.77} \quad (1)$$

$$\text{Initial rate of formation } \left(\frac{dCrO_4}{dt}\right) k_i = k_2 \cdot [H^+]^{1.48} \cdot \{AgO\}^{0.74} \cdot [Cr^{3+}]^{0.32} = k \cdot (X)_i \quad (2)$$

where $\{ \}$ represents a measure of the amount of AgO added and X represents the unknown species considered to be the rate determining reactant in the pseudo first order reaction.

From equation (2) it may be suggested that

$$(X)_i = k_3 \cdot [H^+]^{0.12} \cdot \{AgO\}^{1.5} \cdot [Cr^{3+}]^{0.32} \quad (3)$$

DISCUSSION

Calculations based on stoichiometric equations for the oxidation reactions indicated that only about 14% of the AgO added was used in oxidising manganese(II) to its higher valency state and only about 7% of the AgO added to the chromium solutions was responsible for chromate formation. These calculations show that most of the added AgO was reduced by some secondary process. Because the reaction mixtures effervesced greatly when the AgO was added, and solution of AgO in acid

is known to liberate oxygen,¹² it can be accepted that the process responsible for the reduction of most of the added oxidant is the evolution of oxygen. Because this reaction predominates, any reduction in the rate of oxygen formation must increase the relative amount of manganese or chromium salt oxidised.

The reduction of Ag^{2+} by water to yield oxygen in perchloric acid solutions has been studied by Kirwin and co-workers.⁵ The plot of apparent rate constant against acidity was found to yield a definite minimum at a perchloric acid concentration of 3.0M. This is the acid concentration at which oxidation of manganese and chromium salts was most efficient (Fig. 1). The rate of oxygen formation in perchloric acid solutions was found to be second order in respect of $[\text{Ag}^{2+}]$, inversely proportional to $[\text{Ag}^+][\text{H}^+]^2$ and related in a complex way to $[\text{ClO}_4^-]$. The increased yield of oxidised manganese and chromium salts observed on the addition of Ag^+ to the solutions (Fig. 3) can thus be attributed to the inhibition of the oxygen formation process. The effect of excess AgO (Fig. 2) may also be explained in part by the higher concentrations of Ag^+ formed on reduction of the excess oxidant.

The rate equation relating the evolution of oxygen to amount of AgO added is more complex than the equations obtained for solutions of silver(II) ion. Not only does dissolution of the solid in acid yield decreasing amounts of Ag^{2+} , but during the course of the reaction increasing amounts of the inhibiting species Ag^+ are formed. The mathematical expression obtained in a study of oxygen liberation on the addition of AgO to sulphuric acid solutions had the form¹³

$$d\text{O}_2/dt = K \cdot [\text{H}^+]^{0.24} \cdot \{\text{AgO}\}^{0.6} \quad (4)$$

The rate of oxygen formation became very slow at pH values approaching 3 and this would explain the marked increase in permanganate and chromate yields in solutions which were 0.1–0.2M in respect of perchloric acid. (Fig. 1).

An increase in temperature has a greater influence on the oxygen liberation process than on the other oxidation mechanisms. This is demonstrated by the effect of temperature on the amount of metal ion oxidised (Fig. 4).

The results recorded in Figs. 1–4 cannot be explained entirely on the basis of the influence of the various factors on the rate of oxygen formation, because, as indicated by equation (2), the rate of chromate formation is itself a complex function of at least three variables. The existence of the fractional terms indicates that the mechanism is complex and that each species may be involved in more than one reaction.

The oxidation of the chromium and manganese ions could occur in solution or on the surface of the solid. The production of chromate or permanganate in solution requires multiple collisions between higher valency silver ions and a hydrated chromium or manganese ion, and although this is feasible, reaction on the solid surface appears more probable. The initial rate of chromate formation was nearly linear in respect to the amount of solid added (Table I) for a given set of conditions, and this tends to support the idea of a surface reaction, because this relationship has been found to apply to heterogeneous reactions involving a species in solution and a solid catalyst.¹⁴ A surface mechanism has previously been proposed to explain the oxidation of ammoniacal solutions by silver(II) oxide.¹⁵

Using the model of a heterogeneous reaction, the unknown species X can be considered to be an intermediate formed on the surface of the solid. From equation (3), the concentration of X is related to $[\text{H}^+]^{0.1} \cdot \{\text{AgO}\}^{1.5} \cdot [\text{Cr}^{3+}]^{0.3}$. The power in

respect of Cr^{3+} can be explained in terms of an adsorption isotherm for this species on the surface of the solid; the small power term in respect of $[\text{H}^+]$ could arise from solution of Ag_2O residues on the surface or from suppression of hydrolysis of the chromium ion; and the fractional power in respect of AgO may merely reflect particle size variation in the solid. Because of the limited solubility of silver chromate, desorption of the oxidised product could be a rate-controlling step. Solution of the silver chromate would be retarded by univalent silver ions in solution and accelerated by protons. Such reactions are in agreement with the terms $[\text{H}^+]^{1.36} \cdot \{\text{AgO}\}^{-0.77}$ found in the expression related to apparent rate constants [equation (1)].

CONCLUSIONS

Manganese and chromium salts can be quantitatively oxidised by the addition of excess silver(II) oxide, and the amount of excess required can be reduced greatly if the rate of the competing reaction, namely the liberation of oxygen, is reduced to a minimum.

The rate of oxygen liberation in nitric acid solutions is much slower than in sulphuric or perchloric acid,⁴ hence the 2–5*M* nitric acid medium proposed by Lingane and Davis⁷ is preferable on these grounds to the sulphuric acid solutions used by the earlier workers.^{8–10} On the other hand, it is necessary to warm the nitric acid solutions to destroy excess reagent present as silver(II) nitrate complexes. It is also desirable to avoid the presence of nitric acid in oxidation-reduction titrations.

To use sulphuric or perchloric acid as the reaction medium requires alternative methods of retarding oxygen liberation. Methods available include lowering the temperature to a minimum, lowering the acidity, or adding univalent silver ion to the solution. Variation of the first two of these factors tends to increase the time required for oxidation, and therefore the preliminary addition of silver ion has much to recommend it. On the assumption that the reaction is a surface process, greater efficiency of oxidation should also result from smaller particle size for the AgO and more vigorous stirring.

It must be emphasised at this point that the efficiency of excess silver(II) oxide in oxidising manganous and chromic salts was clearly demonstrated by Lingane and Davis.⁷ Because excess reagent can be destroyed by warming the solution, the method is preferable to that using sodium bismuthate, where excess has to be removed by filtration, and is preferable to the use of ammonium persulphate with silver ion as catalyst because in this case excess persulphate ion has to be destroyed by boiling.

The theoretical study described in this paper gives some information on the mechanism of the oxidation process and suggests ways in which the amount of silver(II) oxide required to give the desired excess can be reduced, but it should not deter workers from using the method of Lingane and Davis, who solved the problems described in this paper in a practical manner.

Zusammenfassung—Die Oxydation von Mangan(II)- und Chrom(III)-Lösungen durch Silber(II)-oxyd in überchlorsaurer Lösung wurde untersucht. Ausbeute und Geschwindigkeit der Oxydation ändern sich mit der Konzentration des Reduktionsmittels, der zugesetzten AgO -Menge, Temperatur, und Konzentration von Säure und einwertigen Silber in der Lösung. Schlechte Ausbeuten bei der Oxydation können der Bildung von Sauerstoff zugeschrieben werden.

Die Ergebnisse werden im Sinne eines möglichen Reaktionsmechanismus diskutiert und die besten Arbeitsbedingungen für Oxydationen mit AgO angegeben.

Résumé—On a étudié l'oxydation de solutions de manganèse(II) et chrome(III) par l'oxyde d'argent(II) en milieu acide perchlorique. On a trouvé que l'efficacité, et la vitesse du processus d'oxydation, varient toutes deux avec la concentration du réducteur, la quantité d'AgO ajouté, la température, l'acidité, et la concentration en ions argent monovalent dans la solution. L'inefficacité du procédé d'oxydation peut être attribuée à la formation simultanée d'oxygène. On discute des résultats du point de vue mécanisme réactionnel possible, et indique les conditions optimales pour les oxydations utilisant AgO.

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SOME PROBLEMS IN THE ANALYSIS OF GASEOUS DECOMPOSITION PRODUCTS*

A CRITICAL EVALUATION

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Summary—Whether the analysis of effluent gases during thermal decompositions is used to elucidate the progress or the mechanism of the decompositions, or to characterise the specimen, certain problems must be dealt with. These problems, involving heating, the analysis of the products, and the compromises which must be made in simultaneous measurements, are discussed.

INTRODUCTION

THE analysis of effluent gases during thermal decompositions can be of great help in elucidating the progress or the mechanism of the decomposition. In some cases, too, the decomposition products may be used to characterise or identify the specimen. For whatever purpose the analysis is carried out, certain problems must be overcome. These problems relate to the heating, to the analysis of the products and to the compromises which must be made in simultaneous measurements.

HEATING OF SPECIMENS

The solid material being studied has been or can be heated in several ways, and for multiple-purpose studies as well as specifically for the analysis of the decomposition products. The most common of the multiple determinations would be simultaneous differential thermal analysis and effluence analysis; the effluence from a thermogravimetric analysis could also be analysed, but this will invariably be accompanied by considerable dilution. In any event, in such simultaneous determinations the heating programme and heating conditions are fairly rigidly prescribed by the requirements of the other technique. In those cases in which the sample is heated specifically for analysis of gaseous decomposition products, a fairly wide range of heating conditions can be and have been used. Examples could include slow heating of a rather massive sample to some fixed temperature or, at the other extreme, flash heating by use of a high-intensity source of visible and infrared radiation. A common technique, intermediate between these, is the practice of placing the sample on a heater (wire) or in a heater specially formed, then applying a predetermined voltage to the heater so that the specimen heats in an uncontrolled but approximately reproducible manner. In contrast to this latter, the specimen can be heated in some programmed manner, as would be typical in the simultaneous determinations.

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SIMULTANEOUS DETERMINATIONS

Let us use as a starting point the present author's work with some simultaneous determinations. This has been, of late, generally concerned with some form of thermal analysis, so that simultaneous differential thermal analysis and effluence analysis would have obvious benefits. In previously reported work,¹ the author has connected a dynamic-atmosphere differential thermal analyser to various devices for detecting gaseous products and/or establishing the nature of the products.

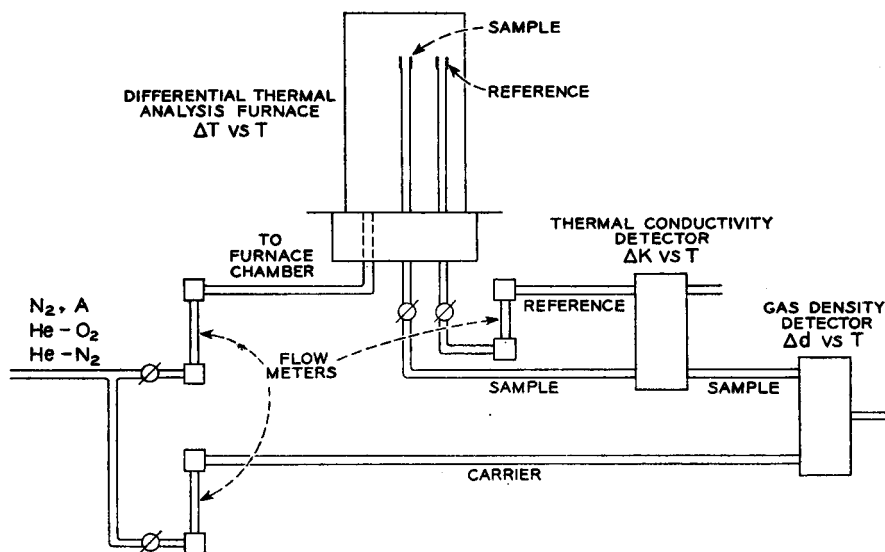


FIG. 1.—Combination differential thermal analysis and double effluence analysis. The transient changes in the sample stream are detected in chromatographic-type analysers.

One arrangement used is shown in Fig. 1. In this arrangement a gas is supplied to the furnace chamber under sufficient pressure to cause a reasonable flow—this flow varies with the type of experiment—downward through the sample and through the reference materials. The gas passing through the reference is used as the reference gas in the thermal conductivity detector, and the gas passing through the sample is compared with it. Any gaseous decomposition product whose thermal conductivity is different from that of the “chamber gas” will then produce in the thermal conductivity detector a different cooling effect from that produced by the pure chamber gas during the time that the product gas is passing through the thermal conductivity detector. The magnitude of the differential signal from the thermal conductivity detector is, at low concentrations, proportional to the quantity of the product gas passing through at the moment, so that integration of the area under a total deflection is a measure of the quantity of the gas evolved, provided that the nature of the gas is known. In this arrangement, the gas which has passed through the sample then goes into the gas density detector. The gas density detector has the advantage (over the thermal conductivity detector) that it is not only a quantitative measuring device, but is to some extent qualitative. It has a further advantage that the sensitivity of the detection can be adjusted by judicious selection of carrier gas, because the

density or "apparent molecular weight" is the only property of importance in the measurement.

The gas density detector depends for its operation on the effect of minor changes of flow in the vertical column on the total flow in tubes connected to the top and bottom of a vertical column. Let us assume that in this device (Fig. 1) a steady-state flow of sample and carrier gases into their ports has been established so that we have a steady-state cooling of the detector elements. Now at some point upstream we inject a small quantity of a product gas, as we might in the normal course of a decomposition in differential thermal analysis. If this product gas is heavier than the carrier gas, the change in density, of course, will be an increase and, hence, the sample plus carrier gas will tend to flow downward to a greater extent than upward. This downward flow will decrease slightly the flow in the lower supply tube (Fig. 1 of ref. cited) and increase slightly the flow in the upper supply tube; this change in flow in the supply tubes produces a change in the cooling effect on the detector elements, an increase in the upper and a decrease on the lower. The differential flow at any moment is proportional to the difference in density of the sample plus carrier gas from that of the sample gas alone, permitting, of course, a quantitative measurement of the material passing through (assuming that it is a single gas). Note, however, that the density of the sample plus carrier gas is dependent not only on the quantity of sample but also on the nature of the sample; *i.e.*, that a gas which, pure, is only slightly heavier than the carrier gas will at a given level of concentration produce some fixed differential flow, but a gas substantially heavier than the carrier gas will at the same concentration produce a significantly greater differential flow. Because of this, qualitative as well as quantitative information can be obtained. If the sample gas is unknown, a second experiment with a carrier gas of different density will provide results for calculation of the real or apparent molecular weight of the sample. (If the sample is a mixture of gases, the apparent density will be dependent on their relative proportions and their relative densities in the pure state.) If the number of possibilities is quite limited, a simpler identification is possible by bracketing the density of the suspected gas in two runs; for example, if there is reason to believe that the specimen gives off oxygen when heated in an inert atmosphere, an experiment using nitrogen as the carrier gas will show that the sample is more dense, and a second experiment using argon will show that the sample gas is less dense; if necessary, direct comparison of the areas will show whether or not the apparent molecular weight of the gas is 32.

The present author has used this type of identification in several cases of which two may be cited. In some studies of cobalt oxalate hydrate the nature of the second step was not known with certainty. Most oxalates decompose in a non-oxidising atmosphere by loss of carbon monoxide to go to the corresponding carbonate. A cobalt oxalate resulting from the heating of the dihydrate decomposed *ca.* 400° to yield what appeared to be a finely divided metal. In closed-chamber differential thermal analysis experiments with air as the furnace atmosphere, this metal powder had, around the opening along the support tube, evidence of oxide formation. The question was resolved by differential density analysis using nitrogen as the carrier gas. If the cobalt oxalate decomposes directly to the metal, 2 moles of carbon dioxide are released and because 2 moles of water are also released the areas should be in direct relation to the density difference. The density difference between water

and nitrogen, assuming ideal gas, *etc.*, is 28–18 or 10 g per mole; the difference between carbon dioxide and nitrogen would be 44–28 or 16 g per mole. The ratio of areas then should be 1.6 if the decomposition is directly to the metal. Within a few percent, attributable to experimental error, this is the result obtained. Note that in this experiment carbon monoxide, having a molecular weight of 28, would not have shown its presence at all, because its density is the same as that of nitrogen.

As part of the same work, nitrogen and argon were used to establish the evolution of oxygen during the decomposition of lanthanum oxalate hydrate. Some carbon had been found with the lanthanum oxide when the material was heated in an inert atmosphere. Above 700° a gas heavier than nitrogen, but lighter than argon, was evolved. In another experiment, reported therein but using oxygen as the dynamic gas, the arrangement shown in Fig. 1 was used to obtain simultaneous measurements of ΔT , Δd and ΔK as lanthanum oxalate hydrate was decomposed. The thermal conductivity measurements are not very useful, because carbon monoxide does not differ enough from oxygen. Carbon dioxide could be detected, but not with nearly the sensitivity obtainable in a helium or hydrogen stream.

Although these particular sets of curves were obtained during single runs with all measurements being made simultaneously, this is not by any means a necessary procedure. Separate experiments would be just as instructive, and possibly experimentally more convenient, so long as they were planned properly.

GAS CHROMATOGRAPHY

In many cases a more specific identification than described above may be needed, because at some stages in the decomposition more than one product may be given off. For such cases, the addition of gas chromatography is useful. Gas chromatography, as ordinarily practised, would be relatively ineffective; it would measure all the decomposition products up to the time of sampling. Specific identification of the product of a particular reaction requires that the sampling be made for that reaction alone; *i.e.*, any reaction products from previous decompositions should already have been removed from the site of sampling. This can be done readily by an arrangement such as that shown in Fig. 2. In this system a furnace like that shown in Fig. 1 is used to carry out the thermal decomposition. The carrier gas which passes through the sample, may, if desired, be passed through a thermal conductivity cell for a continuous and general survey of decomposition products, but, more important, it passes through a pair of sampling valves with, in some cases, an interposed water trap. These sampling valves operate at programmed intervals to withdraw samples of gas from the stream and pass them through chromatographic columns and detectors. The programming is done by trial and error. For the Fluoropak column, and separately for the split column flow, conditions were determined which gave adequate separation. An adjustable cam timer was then connected to the sampling valves so that during each revolution one sampling valve would open for 5 sec, then close. The oven temperature, the flow rates and the sampling times were chosen for each type of experiment specifically to permit rapid sampling. In effect, each sampling occurs soon after the last expected peak from the previous sampling.

The Fluoropak column, when used, permits all non-polar and not very polar materials to run through rapidly, but holds up the water long enough to give separation and permit measurement.

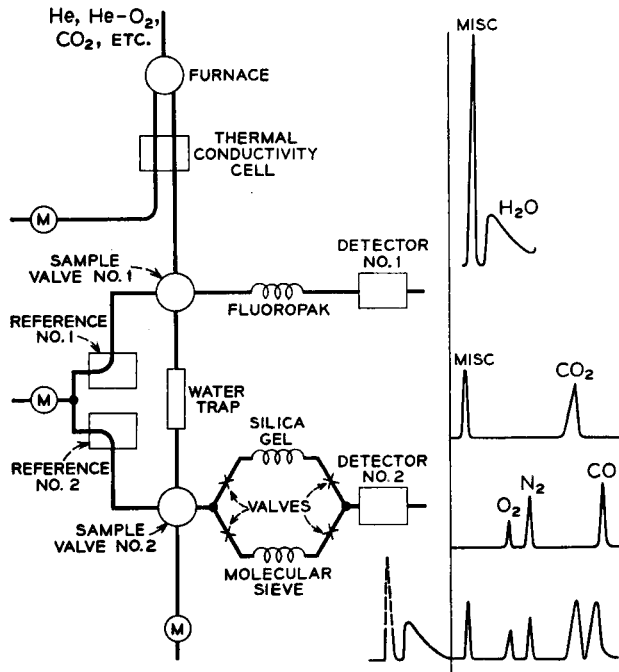


FIG. 2.—Gas train and switching for repetitive dual-sampling chromatography. Sample valve No. 1 transfers a 3-ml sample and No. 2 a 5-ml sample. Sampling interruptions have been deleted in copying (see Fig. 3.)

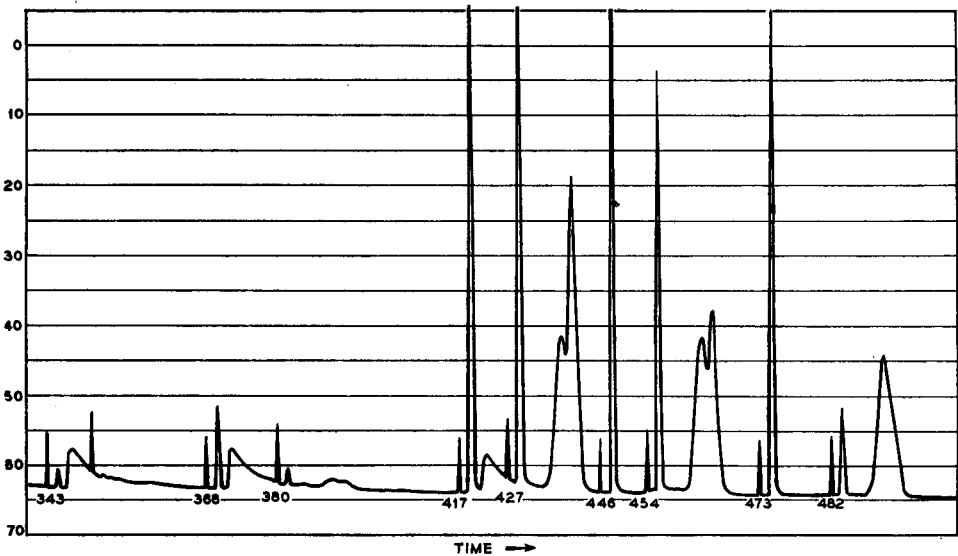


FIG. 3.—Chart section showing a number of sampling cycles and the temperature at which the sample was taken.

The temperature at the moment of sampling is measured and the reaction occurring at that temperature thus described. Alternate samplings, *e.g.*, 417° and 446°, are into the Fluoropak column; the others go through the split column.

The second sampling valve in turn withdraws a specimen from the stream and directs it through a split column to a second detector. This split column has silica gel in the one side and a molecular sieve in the other; the silica gel holds up the carbon dioxide but passes the other permanent gases through rapidly, and the molecular sieve separates the permanent gases. Proper adjustment of the relative flows permits appearance of the carbon dioxide conveniently in the interval of time between the appearance of nitrogen and of carbon monoxide from the molecular sieve. The chromatogram results from the presence of all the gases, but is shown at the right for each column and at the bottom for a complete cycle. Fig. 3 shows a chart section with a number of cycles, the appearance and disappearance of peaks reflecting the beginning and subsidence of reactions as the specimen material is heated.

Examination of several cycles of the chromatographic analysis permits, then, the following of a reaction or, more important, a series of reactions by the relative heights or areas of peaks. Fig. 4 shows such a series. The left-hand analyses are solely for water; those to their immediate right are the associated samplings for the permanent gases and those at the far right a subsequent series of analyses for the permanent gases. No water appeared in the later analyses for water so these are not shown. Note that even in the water analysis an indication of the increasing concentration of other gases was apparent from the growth of the peak just before the rather broad water peak. Similarly, even though the carbon dioxide and carbon monoxide peaks run together at high concentrations, the sharp peak shortly after the sampling, resulting from the permanent gases other than carbon dioxide passing rapidly through the silica gel column, gives an indication of the concentration of carbon monoxide even when the peak is almost obscured by the carbon dioxide. At the higher temperatures, carbon dioxide evolution ceases and carbon monoxide is the only product detected.

The results from one run are tabulated in Fig. 5 along with the differential thermal analysis and differential conductivity curves. The water is given off over a rather wide range, and the peaks are poorly defined in this dynamic atmosphere of helium; then the decomposition of oxalate occurs very sharply, and the interrupted peak on the thermal-conductivity curve can be related to the more or less continual evolution of carbon dioxide coupled with the quickly-terminated evolution of carbon monoxide. The new appearance of carbon monoxide at higher temperatures is also apparent. The high drift in the differential thermal analysis signal is a result of sintering of the specimen and consequent change in the heat transfer from the side to the centre of the specimen. One might conclude from these particular curves that ΔK is a more sensitive measurement than ΔT , and in some cases this could be justified. Consider, however, that this particular experiment used a helium atmosphere and the thermal conductivity change is at a maximum; a dynamic atmosphere of helium would seldom be picked for differential thermal analysis (*vide infra*). Further, differential thermal analysis detects changes of state which the thermal conductivity of the gas stream obviously cannot reflect.

Some of the earlier exploratory work combining chromatography with differential thermal analysis shows the hazard of vitiating results from one of the techniques. Fig. 6 shows some differential thermal analysis curves for an ocean sediment specimen obtained with air and with helium as dynamic atmospheres. While the analysis in helium was being performed, a technician took chromatographic samples by manual

operation of a sampling valve at regular intervals.² There is no difficulty in following the appearance of carbon monoxide and the appearance and virtual disappearance of carbon dioxide in the decomposition products, but there is significant difficulty in finding any thermal effects in the helium run to which to relate the gas evolution.

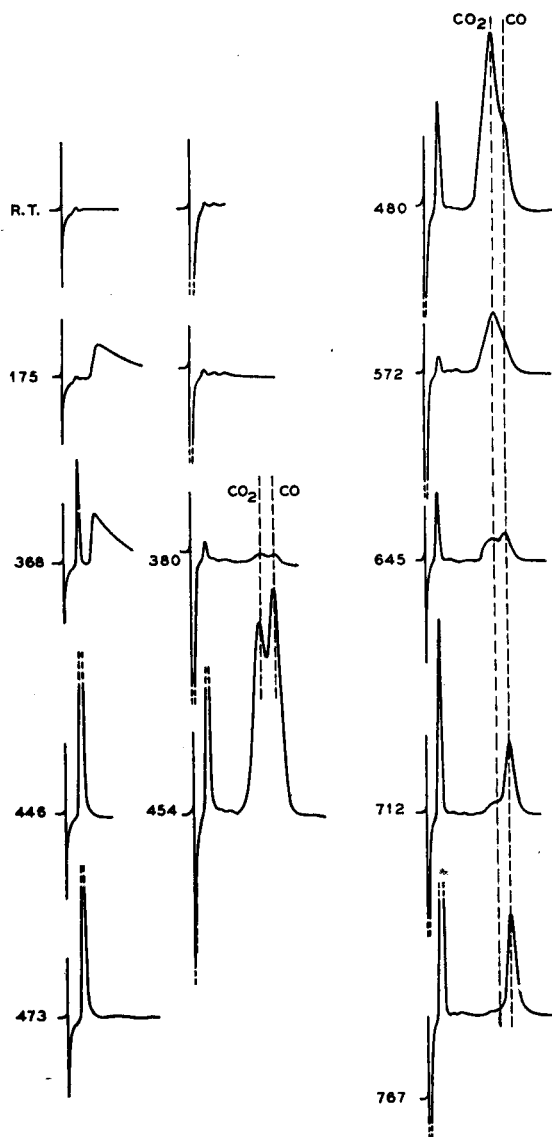


FIG. 4.—Reproduction of several chromatographic analyses from the chart of which Fig. 3 showed a part. The temperatures of sampling are indicated. The appearance and disappearance of specific products can be followed easily.

One may not conclude that combinations of techniques will necessarily be useful. Simultaneous determinations are of benefit only under those conditions in which neither technique is greatly compromised. The planning of separate experiments for each technique will often be more fruitful.

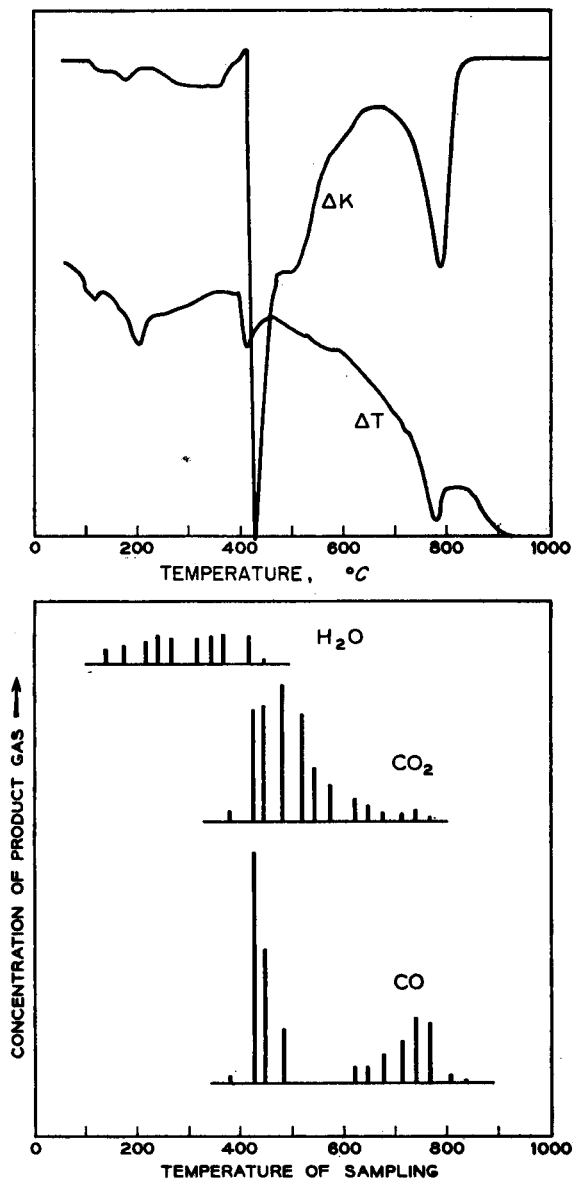


FIG. 5.—Tabulated chromatographic peak heights related to the simultaneously-obtained differential thermal analysis and thermal conductivity analysis of the effluent stream.

The sudden appearance of carbon monoxide and dioxide is indicated also by the plots. The curves, however, give no hint of the relative amounts of CO_2 and CO .

CRITIQUE

With all the problems of simultaneous analysis, and the distinct probability that separate experiments could be better or more instructive, the simultaneous-determinations technique is generally superior to point-by-point sampling for the same types of analyses. Let us consider the technique devised by Murphy, Hill and Schacher³ in which a differential thermal analysis was performed of poly(vinyl chloride) in an evacuated vessel which had connections also to some previously evacuated sampling tubes for mass spectrometry. The object is, of course, to determine

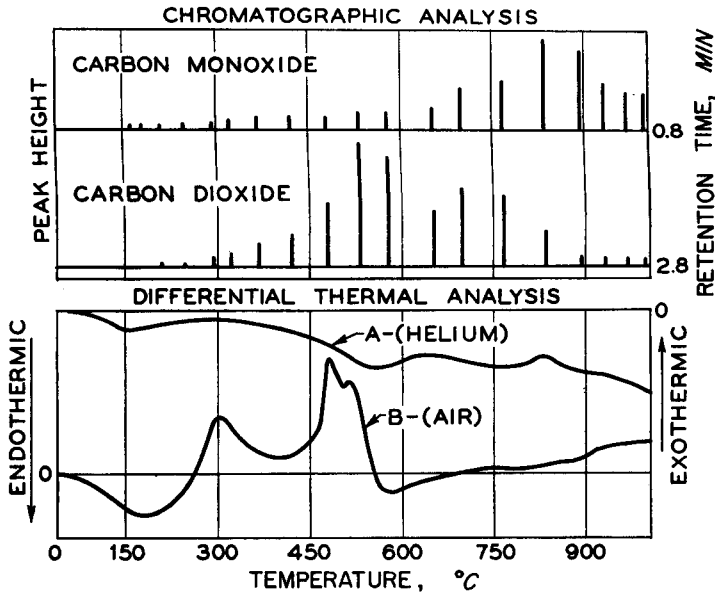


FIG. 6.—Differential thermal analyses of an ocean sediment related to the effluence analysis. The appearance and disappearance of the gases can be related to the peaks of curve A, but curve B bears no appreciable resemblance because the reactions are quite different.

the identity of the gaseous products coming off at various stages of the heating, but consider the required procedure. One must first make a trial run in order to establish the temperatures which may be of interest. After selecting the sampling temperatures a re-run must be made with operator monitoring in order that the selected samples may be taken at the proper time; and finally, the gaseous samples taken must be conveyed to the other instrument, in this case a mass spectrometer, and analysed individually. All of this is perfectly possible, and may be justified on the basis of the need for information about a particular sample; but there immediately arises the problem of the need for an operator to make a judgment on probably inadequate results. That is, on a specimen with which the operator is not familiar, a single thermogram is seldom sufficient to establish the identity of a given reaction.

In this technique the choice of sampling points is obviously extremely important, yet the example shown by Murphy *et al.*, involves what is apparently an error in choice. They sampled at 300 and 400°, the lower temperature being at the peak of

an endothermic reaction and the higher temperature at what they describe as a flat exotherm. They found, as they expected, hydrogen chloride evolved at 300°; and we may infer that they had expected similar evolution at 400° for they reported that no hydrogen chloride was evolved, without specifying the presence or absence of any other material. The absence of any material evolved in the 400° region should not be a surprise; that region is almost certainly not an exotherm or caused by any reaction at all. It is far more likely a simple change in base line resulting from the change in thermal properties of the specimen. The important point here is not that their information needs re-interpretation, but that such an error is easily possible with point-by-point sampling techniques.

Let us now consider an arrangement in which the gas given off by a heated specimen is swept by a carrier gas into a thermal conductivity detector. In the arrangement described by Ayres and Bens,⁴ the sample cells are test-tubes set in a metal block. A differential thermal analysis is performed on the specimen, and the plot from the thermal conductivity cell is related to the differential thermal analysis plot. The carrier gas passes through a preheater and then flows over the sample and reference specimens and thence into the detector cell; note that the gas does not pass *through* the specimen, so the atmosphere surrounding the particles will vary depending on the nature of the product gas and the depth of the particle within the total specimen. The upper layers are continually exposed to an atmosphere of essentially pure helium, but, during a decomposition, the helium will be displaced by the product gas and, especially near the bottom, the particle will experience an enrichment of the product gas concentration.

The effect of the enrichment within the bulk of the specimen will vary, depending on the nature of the sample. Reactions having any appreciable semblance of reversibility will be spread over a range of temperatures because of the atmospheric effect, but yet not to the same extent as would be the case in the absence of a moving atmosphere, because we can consider any product gas to be diffusing outward into a zero level concentration above the specimen. For a reversible reaction, then, this technique will yield differential thermal analysis curves intermediate between those obtained in static atmospheres and those in dynamic atmospheres, as cited previously. The effluent gas analysis will closely parallel the differential thermal analysis curve. Irreversible decompositions, such as the perchlorate decomposition and many organic decompositions, will be virtually unaffected by any movement of the atmosphere, because these reactions proceed rapidly when the decomposition temperature is reached, regardless of the ambient atmosphere. The detection of the effluent gas can be expected to agree less well than in the case of the reversible reactions, because a tailing off is essentially certain to follow a rapid exothermic reaction; in addition to the effect from burst of gaseous products spewed into the carrier stream, these products displace the carrier gas from the nooks and crannies within the specimen, and some reasonable interval of time will be required for this material to diffuse out of the specimen and into the gas stream. In reversible reactions, under this type of condition, there is very probably a diminution in the rate of formation of the product gases as their concentration increases and, towards the bottom of the sample vessel, material which has not reacted may yet exist after the peak temperature difference has passed. The return to the base line will be slow because of this continuing reaction, and during the same period these last portions of product gases will be diffusing out

of the specimen and into the gas stream in ever-decreasing quantities; the effect in the gas detector is, then, rather similar to the differential thermal analysis peak.

Let us examine the results by Ayres and Bens using ammonium perchlorate, first reviewing the reactions of ammonium perchlorate under a small variety of conditions. Differential thermal analysis curves in various atmospheres were obtained by Stone;⁵ in an ammonia atmosphere the entire decomposition occurs at one temperature, because the presence of the ammonia represses the initial decomposition. In any other gas a preliminary decomposition occurs which is slightly pressure-dependent. The final decomposition temperature remains the same. Note that this initial decomposition is not a *necessary* prelude to the exothermic decomposition. The evidence so far suggests that in the absence of ammonia this initial decomposition comprises the loss of all or part of the ammonia. We might predict either a double salt remaining at this stage or, if all the ammonia is lost, that the perchloric acid vapour pressure has not yet reached 1 atmosphere.

In vacuum the final decomposition is not exothermic at all. We may infer that the ammonium perchlorate decomposition products from the initial reaction volatilise and the material is swept out before decomposition.

In any case, the curve obtained by Ayres and Bens in helium would correspond to the third of Stone's curves, *i.e.*, the one obtained in nitrogen at 1 atmosphere. The difference in the nature of the flowing or dynamic gas between the two experiments is of no consequence, so long as the gas does not enter into any sort of reaction with the specimen. The drawn-out initial decomposition, and the tailing off of the gas evolution after the final decomposition, can be attributed to the manner of passing the gas across the sample as explained above.

Less volatile products will cause a rather different trouble, but the problem is apparently purely physical, and could be corrected by redesign of the apparatus. Ayres and Bens also show decomposition curves for nitroglycerine and a propellant. Note that at the upper extremes in temperature an evolution of gas appears to take place with no evidence of a thermal effect. This is more likely caused by the condensation of a decomposition residue in a cooler part of the glassware and subsequent vaporisation of the residue as the heating continues and that part of the glassware reaches a sufficiently high temperature.

Ayres and Bens called attention to the possible troubles from condensation; the present author's contribution is the delineation of events within the sample.

Another use of simultaneous differential thermal analysis and a form of effluence analysis was of a very special kind. Bussière and others⁶ constructed an apparatus in which they could simultaneously perform differential thermal analysis, thermogravimetric analysis, and a measure of the emanation from radioactive thoron. Their work is based on the absorption of radioactive thoron along the interfaces between crystallites. The sample used was thorium oxalate hydrate. The radioactive decay of thorium produces thoron, (also radioactive), part of which escapes and part of which is trapped in the interfaces or interstices and, at best, moves slowly to the particle surface. When, however, the material undergoes a change of state, the disruption of the crystals permits more ready escape of the thoron from amongst the crystallites.

Bussière *et al.* passed a gas stream across their specimen and into a detector in which the radioactivity of this gas stream (from the thoron) was measured. Their

results are not easily interpreted at first sight. The first dehydration is unambiguous; each of the measurements demonstrates an effect which we can accept as decomposition to the dehydrate, as stated by Bussière and others. The second weight loss and accompanying endotherm are clear enough, but there is no corresponding event in the emanation measurement. Further, in the final decomposition, not only does the thermogravimetric curve indicate a single, smooth-wave loss while the differential thermal analysis curve shows a pair of reactions, but the emanation curve even shows a decrease rather than the predicted increase.

The two-step final endotherm shown by the differential thermal analysis could be the decomposition of the oxalate, first to the carbonate, and subsequently to the oxide. On moderately large specimens, and with no *useful* atmosphere control, these two decompositions will (or at least can) overlap enough to give a single thermogravimetric weight loss. The present author will not attempt to explain the slow rise in the emanation between about 120 to 250°. The decrease in the region of 300° may possibly be the result of dilution; the evolution of the other gases may become such a significant part of the total gas flow that the flow through the counter is increased, and the quantity of thoron present in the counter at any moment consequently decreased. As the rapid evolution diminishes, the increased concentration is again apparent. The method is interesting, and may be particularly useful in special cases. As a general technique, it suffers from the disadvantages that it does not provide a complete and unambiguous response to events in the specimen and, further, it requires the presence of thorium or some other radioactive material producing a radioactive gas with a short half-life.

DETERMINATION ONLY OF GASEOUS PRODUCTS

Let us now consider some experiments in which the gathering of information was confined to study of the gaseous products of decompositions. These range from systems in which only the event is of interest to systems in which the products are measured quite specifically, both qualitatively and quantitatively. One of the former type is that of Rogers and others⁷ in which the specimen was pyrolysed in a stream of helium. The organic vapours from the pyrolysis chamber are oxidised to water and carbon dioxide in the combustion tube, to avoid condensation as well as to enhance sensitivity. (The conversion of a molecule of some fairly complex organic material to many molecules of carbon dioxide and water will quite naturally enhance the signal obtained in passing through the thermal conductivity cell.) The pyrolysis block is heated by commercial cartridge heaters through a temperature programme. The results obtained from the thermal conductivity measurements are simple indications of decompositions without identification, except, in some cases, by the temperature at which the decomposition occurs. It has the advantage over the Ayres and Bens apparatus that the conversion to carbon dioxide and water rids the system of easily condensable materials which might later vaporise and give a false signal.

These simple indications of decompositions are useful principally in establishing temperatures of decomposition, but with known products the technique can also be used as a quantitative measure with the same confidence as gas chromatography, because the same type of detector is used. The user must know the product gases specifically, or at least know that the same material containing the same proportions

of carbon and hydrogen will come off from each sample tested. If this knowledge is not available with certainty, more detailed analyses may be in order. It is necessary only to substitute a technique for analysis instead of, or as well as, detection of the gaseous products. There is no reason why programming of the temperature is not still possible. The most generally useful technique for analysis of these effluent gases is gas chromatography; in the reported work seen by the present author, these sample materials have been vaporised into the carrier gas stream, and carried immediately into the chromatographic column.

QUALITATIVE IDENTIFICATION OF DECOMPOSITION PRODUCTS

In general, direct injection of the decomposition product gases into the chromatograph is done by rapidly heating the material in the gas stream, the means of heating being usually the sample container as well. Experimenters principally interested in the chromatographic analysis can very easily overlook the importance of the manner of heating and, indeed, this is a common occurrence. The specimens are heated rapidly, so that the product gases appear in the chromatograph as a single pulse of gases; identification of the gases given off at intermediate temperatures is not attempted.

The transfer of heat from the heater wire to the sample material is a source of variation and error with specimens of appreciable thickness. Jennings and Dimick⁸ avoided the heat transfer problem by evaporating the specimen on the heater wire (using aqueous phosphoric acid to supply hydrogen and oxygen for the decomposition reaction). They examined the effect of temperatures from 550 to 1100°, finding that for thymine there was no appreciable difference in the pyrolysis pattern, *i.e.*, the identities and relative quantities of products. The first composite peak in their Fig. 2 is likely to be permanent gases. These results show their reproducibility on repetition of the experiment as indicated in their table. This is not the sort of reproducibility one would expect from an ordinary chromatographic analysis, so that the deviation of irreproducibility must be related to the pyrolysis technique. The non-linearity in Jennings and Dimick's calibration values may still possibly be a heat transfer problem; the thin specimens with good exposure to the atmosphere may partly volatilise without decomposition, but the thicker specimens, being heated from the inside, may be subject only to the same absolute quantity of vaporisation, and hence a smaller percentage effect. The probability that the thicker specimens reach higher temperatures locally may also lead to some variation in the relative quantities of the several products, even though the identities of the products remain the same. Note that Jennings and Dimick were able to distinguish quite clearly between positional isomers; cytosine and isocytosine showed quite different proportions of products under similar pyrolysis conditions.

Quite different heating conditions were used by Strassburger, Brauer, Tryon and Forziati;⁹ these authors used a much lower temperature pyrolysis in their studies of methyl methacrylate copolymers. They heated their pyrolysis coil to about 450° with 10–15 mg of specimen contained therein. At that temperature, and in the absence of oxygen or of hydrogen, a relatively non-volatile residue is formed. The reactions causing the formation of the residue also introduce distinct non-linearities into the calibration for quantitative measurements so that, for example, the sample

weight-to-peak area ratio varies by a factor of 2 in the methyl methacrylate-ethylene dimethacrylate copolymer.

DEPENDENCE OF PRODUCTS ON CONDITIONS

Although some of the authors cited indicate that the pyrolysis products are the same over a wide range of pyrolysis conditions, to assume this happy circumstance for any given material to be studied would be exceedingly optimistic. A thin layer of material in contact with a heating element or other form of hot surface, at a temperature approximating the ultimate decomposition temperature of the material, may transmit heat rapidly enough to permit the entire film to decompose at essentially the same time, and more or less at the same temperature. The material in contact with the heated surface does not necessarily rise in temperature greatly above the surface of the film. If this heated surface were several hundred degrees, say, above the ultimate decomposition temperature, rapid decomposition of the inner portion of the film could change the conditions of heat transfer substantially. With very thin specimens the problem will arise only in the extreme cases, because the heating of the surface is not instantaneous; the heat capacity of the wire itself will cause some delay in reaching the final temperature, permitting a similar smooth rise by the specimen material.

If a thick sample is placed in contact with a heating element, and the heating element is supplied with a sudden application of an electric circuit, the relatively low thermal conductivity of the typical organic specimen will permit the establishment of a high (and not necessarily continuous) temperature gradient through the specimen. The over-all effect will depend on the nature of the sample-holding system; if the material has been deposited on a wire or other surface by evaporation of a solvent, so that there is a continuous layer on the heating surface, the material next to the heating surface may well be heated slowly enough to permit low temperature decomposition products to form; but these decomposition products cannot escape and will consequently be subject to further decomposition. If particles are laid upon the heating surface, the portion of the surface initially in contact may be heated slowly enough to undergo a low temperature decomposition, but the new layers of material subsequently touching the heated surface are coming in contact with a hotter and hotter surface, bringing about the possibility of a different decomposition mechanism.

The change in products obtained with change of pyrolysis conditions has been demonstrated by Martin and Ramstad,¹⁰ who used flash pyrolysis to decompose cellulose in the sample chamber of a two-stage column. They separated the permanent gases on a gas-solid absorption column, using polypropylene glycol. The specimen was heated by flash photolysis; *i.e.*, intense radiation from a flash tube or arc source was directed on the specimen for a short length of time, the temperature reached depending both on the intensity and the time of exposure. They induced momentary temperatures in the sample in excess of 600°, with intense radiation of a millisecond duration, and compared the results with a slower pyrolysis in the 250–350° range, induced by less-intense radiation lasting for several seconds. The decomposition products are carried into the polypropylene glycol column, where the permanent gases are impeded only slightly. These are led from the glycol column into the activated charcoal column where the gases are separated, the columns being

uncoupled immediately after passage of the permanent gases from stage 1 into stage 2. The slow pyrolysis produces only carbon monoxide and carbon dioxide among the permanent gases, but the flash pyrolysis produces significant quantities of the lighter hydrocarbons. The principal feature of the partition column curves is the greatly diminished amount of water relative to the other components in the flash pyrolysis. Although it is the major component, two of the other peaks at least surpass it in height. Note, too, that the magnitude of the carbon monoxide peak in the flash pyrolysis is more than ten times as high as the carbon dioxide peak, but in the slow pyrolysis it is somewhat smaller. Explanation of these variations would require further knowledge of the system, but a safe general conclusion can be stated: variations in the rate of heating of an organic specimen may cause different products or different relative quantities of products.

OTHER POSSIBILITIES

Now let us consider some of the extensions of effluence analysis. First of all let us consider changes in the carrier gas, made with the intention of encouraging or inhibiting some particular reaction. The use of helium-oxygen and helium-nitrogen mixtures has already been discussed in relation to determining the steps of an inorganic reaction. In this case, the helium-oxygen mixture permitted the oxidation of carbon monoxide, but the absence of oxygen brought about decomposition without oxidation. Similarly, small quantities of oxygen in the carrier gas stream would permit oxidation or partial oxidation of the specimen; or the presence of hydrogen might permit saturation of organic carbon chains. This is not being recommended as a general technique, but as a modification of procedure which might yield useful information. Repetitive sampling into the column in the manner practised by the present author (*vide supra*) would yield successive lots of decomposition products as the temperature was increased. Decompositions of specimens can be carried out directly in the sampling locations of analytical instruments other than chromatographs or chromatographic type of detectors, and similarly the decompositions can be programmed either step-wise or continuously. Two types of analyser are of particular promise, optical and mass spectrometers. Decomposition into, say, an infrared absorption spectrometer sample tube would be of particular interest if a particular compound or functional group were being monitored. Fairly high resolution would be required to obtain unambiguous results. There is the advantage, however, that the appearance of the product could be followed during the entire decomposition and if the decomposition is programmed some measure of the temperatures of appearance of various products may be obtained.

Of the mass spectrometers, the time-of-flight spectrometer would be of special interest because of the high frequency of repetitive sampling possible. Decomposition in a chamber connected to the spectrometer by an appropriate orifice would make possible the gathering of kinetic information on decompositions.

Relating the events recorded by these various techniques needs to be done with great care. Bussière *et al.*⁶ compared curves obtained by their simultaneous determinations (*vide supra*) to those obtained on other (apparently single-purpose) apparatus. Bussière *et al.* conclude that it is preferable to make all the measurements simultaneously in order to obtain agreement in the interpretation of a given reaction. This is a fairly common attitude. The present author has contended¹¹—and still

contends—that unless the results from each technique have some real significance, attempts to relate them are seldom rewarding even when apparently successful. The agreement that is almost unavoidable in simultaneous determinations can give the observer an entirely unwarranted confidence in whatever he chooses the curves to mean. Further discussion of simultaneous determinations is presented in a forthcoming monograph.¹²

Zusammenfassung—Die Analyse der bei thermischen Zersetzungen entwickelten Gase kann dazu dienen, das Fortschreiten oder den Mechanismus der Zersetzungen zu verfolgen oder die zersetzte Probe zu charakterisieren. In jedem Fall müssen bestimmte Probleme berücksichtigt werden. Diese Probleme werden diskutiert, darunter das Vorgehen bei der Aufheizung, die Analyse der Produkte und die Kompromisse, die bei Simultanmessungen geschlossen werden müssen.

Résumé—Que l'analyse des gaz qui se dégagent lors de décompositions thermiques soit utilisée pour élucider le développement ou le mécanisme des décompositions, ou pour caractériser l'échantillon, on doit traiter de certains problèmes. On discute de ces problèmes, comprenant le chauffage, l'analyse des produits, et les compromis auxquels on doit avoir recours lors de mesures simultanées.

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QUENCHOFUOROMETRIC ANALYSIS FOR FLUORANTHENIC HYDROCARBONS IN THE PRESENCE OF OTHER TYPES OF AROMATIC HYDROCARBON

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Summary—In this first paper of a series, a new analytical tool is introduced for the analysis of fluorescent molecules—quenchofluorescence analysis. This field of research will have far-reaching ramifications in organic trace analysis. Analytical use is made of the quenching effect in spectrophotofluorometry. Compounds such as anthracene, phenanthrene, pyrene, benz(*a*)anthracene, benzo(*a*)pyrene, perylene, *etc.*, have been found to be non-fluorescent in nitromethane solution, but hydrocarbons containing the fluoranthenic ring are fluorescent. Use has been made of this phenomenon in characterising fluoranthene and benzo(*k*)fluoranthene in airborne particulates, following column chromatography. The phenomenon has also been used in thin-layer chromatography, directly on the plate.

FLUORESCENCE quenching is a serious problem in the analysis for polynuclear aromatic hydrocarbons in airborne particulates, especially with fairly high solution concentrations of either the compound being analysed or the impurities. Primarily because of this difficulty it was believed that quenching could be a useful analytical tool. With a proper reagent it should be possible to quench part of the fluorescence excitation or emission spectra or all the fluorescence excitation and emission spectra of a molecule. In the former case the quenching could result from the direct absorption of the exciting light by the quencher; in the latter case it could result from the same phenomenon or from formation of a non-fluorescent molecule, or from both. The new molecule could be a complex or a newly formed derivative.

As a first approximation, nitro derivatives, many of which are well-known complexing agents, were selected for investigation for the following reasons. Alcoholic solutions of rhodamine B are quenched to some extent by the addition of nitrobenzene.¹ Aqueous solutions of rhodamine B are completely quenched by picric acid.² Complex formation is believed to cause this phenomenon. Acetone solutions of chrysene are quenched by picric acid and many other nitro compounds.²

Benzo(*a*)pyrene and six other polynuclear aromatic hydrocarbons have been shown to be nonfluorescent in solutions of nitromethane or nitrobenzene.³ Of compounds of this type tetranitromethane was the most potent quencher. The fluorescence of 1 μg of benzo(*a*)pyrene in 10 ml of petroleum ether was completely inhibited by 200 μg of tetranitromethane.³

It is reported that in the presence of bromine, under carefully controlled conditions,

the fluorescence of benzo(*a*)pyrene disappears but that of benzo(*k*)fluoranthene is unaffected.⁴ By this procedure, for which details are not given, benzo(*k*)fluoranthene and benzo(*a*)pyrene were satisfactorily estimated in synthetic mixtures containing equivalent amounts of these two chemicals, perylene, and benzo(*e*)pyrene. The pure spectrum of benzo(*k*)fluoranthene could not be obtained from this mixture.

The selective use of the quenching phenomenon in the analysis for one component in a mixture has been studied in only a few isolated cases, and even in those cases the implications of the general use of quenching to increase greatly the selectivity of many fluorometric methods have not, as yet, been grasped. A thorough study is needed, because quenching reagents can greatly increase the selectivity and usefulness of spectrophotofluorometric and spectrophotophosphorometric analysis for many types of aromatic compound. It is predicted that this type of analysis will have a very wide range of application in organic analysis. It is suggested that these procedures be called *quenchofluorometric* and *quencho-phosphorometric* analysis.

In the work reported in this paper, fluoranthenic hydrocarbons are characterised and determined in the presence of other types of polynuclear aromatic hydrocarbon. In subsequent papers, other types of quenchofluorometric procedures with a very high order of selectivity will be introduced.

Fluoranthenic hydrocarbons such as benzo(*b*)fluoranthene, benzo(*j*)fluoranthene, and indeno(1,3,3-*cd*)pyrene have been reported to be carcinogenic to mice.⁵

EXPERIMENTAL

Reagents and apparatus

Nitromethane was obtained from Matheson, Coleman, and Bell, Cincinnati, Ohio, and distilled before use. Alumina adsorbent was obtained from Brinkman Instruments, Inc., Great Neck, L.I., New York.

All chromatographic plates were examined for fluorescence colours in a Chromato-Vue cabinet (Kensington Scientific Corp., Berkeley, California) under a 3660-Å light source.

The following settings were used with the Aminco-Bowman spectrophotofluorometer: sensitivity 50, meter multiplier 0.01 (whenever possible), slit arrangement No. 2, and phototube RCA type 1 P 21.

Thin-layer chromatographic procedures

A. Plates were prepared and developed by procedures analogous to those described previously.⁶ Where mixtures of an alkane and nitroalkane were used as developing solvents, the plate was read under the ultraviolet light as soon as it was taken out of the tank, and was then read again after it had dried (about 15–30 min).

B. *Nitromethane test for non-quenchable compounds, such as fluoranthenes, etc.* After thin-layer chromatography the line of development is treated with small bursts of nitromethane fumes, or with microdrops of the liquid. This can be done with a throwaway pipette fitted with a squeeze bulb. Any change or loss in fluorescence colour is noted.

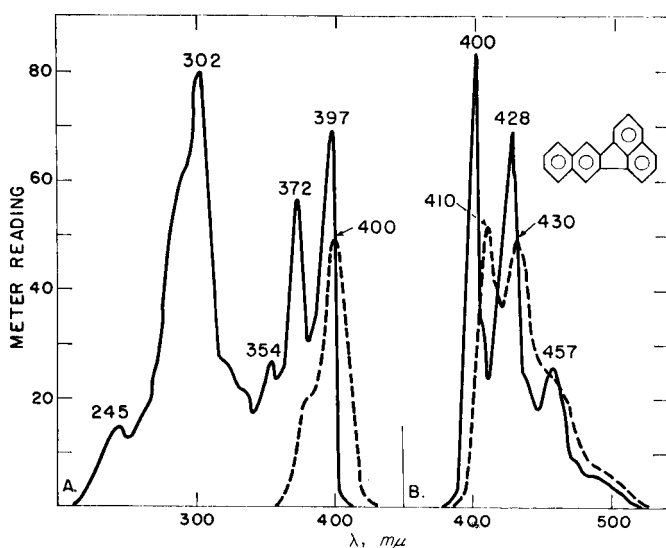
RESULTS

Spectrophotofluorometry

In previous work the fluorescence spectra of a large variety of hydrocarbons were obtained in pentane and sulphuric acid.⁷ One of the main variables in the spectra of these different hydrocarbons was their broad range of intensities. With nitromethane as the solvent most of these hydrocarbons become non-fluorescent, thus greatly increasing the selectivity of the fluorometric procedure. Thus, all non-fluoranthenic hydrocarbons are non-fluorescent in nitromethane (Table I). It must be emphasised that although all the hydrocarbons in Tables I and II are fluorescent in pentane or chloroform solution, only the fluoranthenic hydrocarbons are fluorescent in nitromethane solution.

TABLE I.—COMPOUNDS WHOSE FLUORESCENCE IS QUENCHED IN NITROMETHANE SOLUTION

Acenaphthylene	Triphenylene
Phenanthrene	Benzo(<i>b</i>)chrysene
Anthracene	Benzo(<i>a</i>)pyrene
9-Bromoanthracene	Benzo(<i>e</i>)pyrene
Benzo(<i>a</i>)anthracene	Perylene
11- <i>H</i> -Benzo(<i>a</i>)fluorene	Dibenz(<i>ac</i>)anthracene
11- <i>H</i> -Benzo(<i>b</i>)fluorene	Dibenz(<i>ah</i>)anthracene
7- <i>H</i> -Benzo(<i>c</i>)fluorene	Dibenz(<i>aj</i>)anthracene
Benzo(<i>c</i>)phenanthrene	Picene
Chrysene	Anthanthrene
4- <i>H</i> -Cyclopenta(<i>def</i>)phenanthrene	Benzo(<i>ghi</i>)perylene
Naphthacene	Naphtho(2,1,8- <i>qr</i>)naphthacene
Pyrene	Dibenzo(<i>ae</i>)pyrene
1-Bromopyrene	Dibenzo(<i>gp</i>)chrysene
1-Methylpyrene	Dibenzo(<i>brst</i>)pentaphene

FIG. 1.—Fluorescence spectra of benzo(*k*) fluoranthene.

A. Excitation spectra: at emission λ 400 $m\mu$, MM = 0.01 and 10^{-6} M in pentane (—) and at emission λ 430 $m\mu$, MM = 0.03 and 10^{-5} M in nitromethane (---).

B. Emission spectra: at excitation λ 302 $m\mu$, MM = 0.01 and 10^{-6} M in pentane (—) and at excitation λ 400 $m\mu$, MM = 0.03 and 10^{-5} M in nitromethane (---).

Although these latter hydrocarbons are fluorescent in nitromethane solution, their short-wavelength excitation spectral bands have been quenched (Table II). This latter effect may result from direct absorption of the short-wavelength light by the quencher. The striking effect of nitromethane on the fluorescence spectrum of benzo(*k*)fluoranthene as compared to the spectrum in pentane is shown in Fig. 1. The intensities of all bands have been decreased. The partial quenching of the short-wavelength excitation bands, which probably results to some extent from the internal filter effect of the solvent, merits further investigation. The emission spectral bands, which are present in chloroform or pentane, are present in nitromethane also, although their intensity has been decreased.

TABLE II.—FLUORESCENCE SPECTRA OF FLUORANTHENIC HYDROCARBONS IN NITROMETHANE

Compound	Det. limit, <i>ng/0.1 ml</i>	Molar concn.	Emission spectra ^a		Excitation spectra ^b	
			EM. λ , $m\mu$	MM.T	Exc. λ , $m\mu$	MM.T
Fluoranthene ^{cf}	340	10 ⁻⁴	460	0.65	380	0.68
Benzo(<i>b</i>)fluoranthene ^c	400	10 ⁻⁴	400	0.45	378	0.67
			440			
			450	0.69	390	0.40
				0.63		
Benzo(<i>k</i>)fluoranthene ^{df}	13	10 ⁻⁵	409	2.0	384	0.9
			430	2.0	400	2.0
			458	0.9		
Benzo(<i>ghi</i>)fluoranthene ^{cf}	250	10 ⁻⁴	420	1.1	395	1.3
			445	1.4	410	0.6
			472	0.9		
			500	0.4		
Indeno(1,2,3- <i>cd</i>)pyrene ^{eg}	14	10 ⁻⁵	480	2.0	385	2.5
			500	2.4	408	2.4
					415	2.2
					440	0.8
Indeno(3,2- <i>j</i>)acenaphtho- (1,2- <i>k</i>)fluoranthene ^{df}	7	10 ⁻⁶	474	0.55	390	0.7
			500	0.62	400	0.6
					430	0.3
Diacenaphtho(1,2- <i>j</i> :1',2'- <i>l</i>) fluoranthene ^{eg}	5	10 ⁻⁷	474	0.11	395	0.11
			500	0.12	405	0.10
					430	0.05
Acenaphtho(1,2- <i>b</i>)quinoxaline ^{gh}	750	10 ⁻⁴	494	0.27	397	0.27
Acenaphtho(1,2- <i>b</i>)benzo(<i>f</i>)- quinoxaline ^{gi}	60	10 ⁻⁵	468	0.45	399	0.48
Acenaphtho(1,2- <i>b</i>)benzo(<i>g</i>)- quinoxaline ^{eg}	70	10 ⁻⁵	500	0.42	399	0.42
					403	0.40
Diacenaphtho(1,2- <i>b</i> :1',2'- <i>d</i>)- thiophene ^{dg}	100	10 ⁻⁵	472	0.34	394	0.41
			501	0.41	409	0.38

^a Instrument set at most intense excitation wavelength maximum. Values *in italics* are shoulders.

^b Instrument set at most intense emission wavelength maximum. Values *in italics* are shoulders.

^c Band intensities in nitromethane-trifluoroacetic acid (99:1, v:v) decreased one-half to one-third.

^d Same intensities in acid solution.

^e Intensity doubled in acid solution.

^f Band intensities in nitromethane-triethylamine (99:1, v:v) decreased one-half to one-sixth.

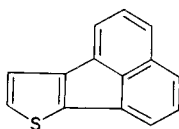
^g Same intensity in alkaline solution.

^h In nitromethane-trifluoroacetic acid (99:1, v:v) at $2 \times 10^{-5}M$: excitation λ max. 400, MM.T 0.67 and emission λ max. 515, MM.T 0.67.

ⁱ In nitromethane-trifluoroacetic acid (99:1, v:v) at $10^{-6}M$: excitation λ max. 423, 450 and MM.T 0.64, 0.70, respectively and emission λ max. 507.

A tentative explanation for the complete quenching of the non-fluoranthenic hydrocarbons is that these compounds form a non-fluorescent π -complex in the excited state. In line with this hypothesis is the fact that naphtho(2,1,8-*qr*)naphthacene is fluorescent in chloroform and non-fluorescent in nitromethane, but its absorption spectra in chloroform and nitromethane are essentially identical from 600 to 370 $m\mu$ (the cut-off point for nitromethane). Consequently a complex is not present in the ground state, but could be present in the excited state (all concentrations were $10^{-5}M$). This hypothesis is being investigated.

Every hydrocarbon so far investigated that is fluorescent in nitromethane solution has a fluoranthenic ring as part of its structure. Even the heterocyclic hydrocarbons appear to follow the same rule. The quinoxaline derivatives have 1 ring in the fluoranthenic part of the molecule with *para*-nitrogen atoms. In spite of these nitrogens, the compounds act like the other fluoranthenic derivatives. In the thiophene compound a true fluoranthenic ring is not present. A sulphur analogue, which is iso- π -electronic to fluoranthene, is present, however, *e.g.*,



Consequently, it appears that a fluoranthene-type ring in a molecule is necessary for a polycyclic aromatic hydrocarbon to be fluorescent in nitromethane. Exceptions to this rule are being sought.

APPLICATION

Characterisation following column chromatography

Following the column-chromatographic fractionation of organic airborne particulates, some of the fluoranthenic compounds can be readily characterised in the various fractions. When the fluorescence spectrum is obtained in nitromethane solution, the interfering aromatic hydrocarbons are eliminated. For example, the interfering spectra of all the other components in the pyrene fraction are eliminated and the fluorescence spectrum of fluoranthene is obtained (Fig. 2).

In the same way, the pure excitation and emission spectra of benzo(*k*)fluoranthene can be obtained from a nitromethane solution of the benzpyrene fraction of organic airborne particulates (Fig. 3). Thus, with a single spectral run in nitromethane, benzo(*k*)fluoranthene can be readily characterised in the benzpyrene fraction.

Characterisation following thin-layer chromatography

The use of nitromethane following a thin-layer chromatographic separation of the benzene-soluble fraction of airborne particulates is shown in Fig. 4c. The fluorescence colours obtained for a dry chromatogram following development are seen in Fig. 4b. Treatment with trifluoroacetic acid fumes gives the chromatogram as shown in Fig. 4a. The brilliant emerald green and pink fluorescent spots (marked 1 and 2) have been found in many of the benzene-soluble fractions of urban airborne

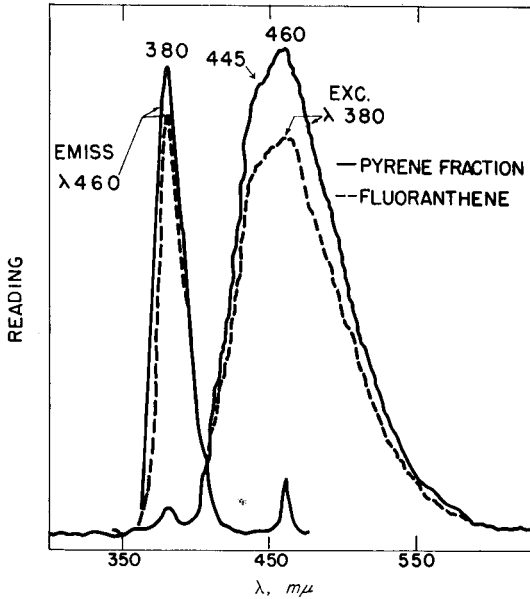


FIG. 2.—Fluorescence spectra of the pyrene fraction of airborne particulates (—) and fluoranthene (----), both in nitromethane.

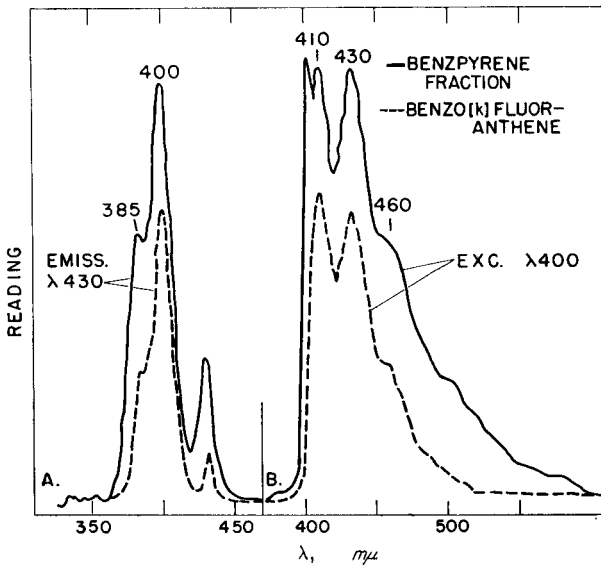


FIG. 3.—Fluorescence spectra of the benzpyrene fraction of airborne particulates (—) and benzo(k)fluoranthene (----), both in nitromethane.

A. Excitation spectra.
 B. Emission spectra.

particulates that have been examined. They serve the function of markers, in that their R_f values denote the relative activity of the alumina or the moving power of the solvent system. Treatment of the original chromatogram with nitromethane quenches the fluorescence of most of the spots, and in addition brings out new spots at 3 and the solvent front. This technique should prove useful in the eventual characterisation of the many unknown aromatic compounds in airborne particulates and other complicated mixtures. When a benzene-soluble fraction is separated on a thin layer of alumina with pentane-2-nitropropane (19 : 1, v : v), the final results differ drastically (Fig. 5a)

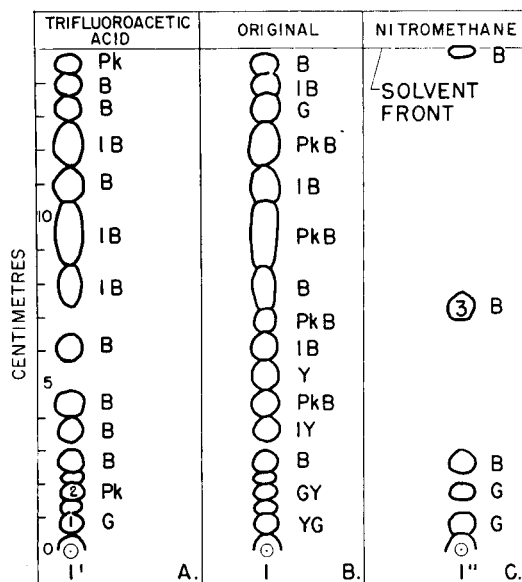


FIG. 4.—Alumina thin-layer chromatogram of a benzene-soluble fraction of airborne particulates.

- A. Original treated with trifluoroacetic acid fumes.
- B. After development with pentane-10% ether.
- C. Original treated with nitromethane fumes.

from the pentane-ether chromatogram (Fig. 4). As the figure shows, hydrocarbons such as benzo(*a*)pyrene are invisible, while benzo(*k*)fluoranthene fluoresces with a brilliant blue colour. On standing, the fluorescence colours of most of the spots change, and new spots appear (Fig. 5b). Thus, evaporation of the nitropropane causes the compounds that are non-fluorescent in nitropropane to become fluorescent. This phenomenon is demonstrated by the benzo(*a*)pyrene spot, which is not seen in Fig. 5a, but which is shown fluorescent in Fig. 5b. Thus, these two different procedures both dependent on the quenching effect of a nitroalkane, can be used in thin-layer chromatography. In addition, either of these procedures can be followed by the treatment with trifluoroacetic acid fumes.

Determination of fluoranthenes

Beer's law type relations were found to hold for fluoranthene in nitromethane from 2 to 25 $\mu\text{g/ml}$ and for benzo(*k*)fluoranthene from 0.2 to 2.5 $\mu\text{g/ml}$. Fluoranthene could be readily determined in a synthetic mixture of equal amounts of pyrene,

fluoranthene, chrysene, and benzo(*a*)anthracene. Similarly, benzo(*k*)fluoranthene could be readily determined in a synthetic mixture of equal amounts of benzo(*a*)pyrene, benzo(*e*)pyrene, perylene and benzo(*k*)fluoranthene. The pure excitation and emission spectra of fluoranthene and benzo(*k*)fluoranthene are obtained from these synthetic mixtures. The procedure involved dissolution of the mixture in nitromethane and then reading of the meter multiplier \times transmittance (M.M.T) values at

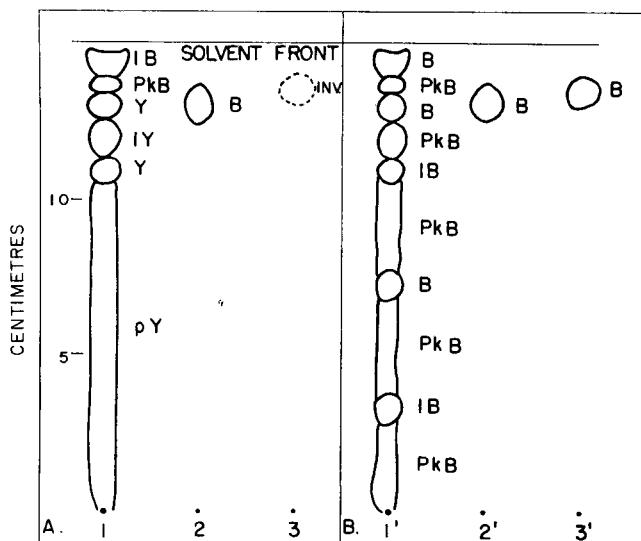


FIG. 5.—Alumina thin-layer chromatogram of (1) benzene-soluble fraction of airborne particulates, (2) benzo(*k*)fluoranthene and (3) benzo(*a*)pyrene.

A. Immediately after development with pentane—5% 2-nitropropane.
B. After plate has dried about 30 min.

the most intense excitation and emission wavelength maxima of fluoranthene or benzo(*k*)fluoranthene. When this procedure was applied to the pyrene fraction obtained after column chromatography of a sample of urban airborne particulates, the values obtained for fluoranthene were 2.5 times those obtained by the ultraviolet absorption base-line method of measurement.^{9,10} Similarly, high values were obtained for benzo(*k*)fluoranthene. Because fractions obtained after the fluoranthene fraction, and just before and after the benzpyrene fraction, were fluorescent in nitromethane solution, it was concluded that either additional fluoranthenic compounds or some other types of unquenched compound were present. The procedure is therefore of value for characterisation but cannot be used for the determination of individual fluoranthenic compounds until better separation is achieved and more information is obtained on any other types of compound that fluoresce in nitromethane solution.

CONCLUSION

A simple technique is introduced that facilitates the characterisation of fluoranthenic compounds following chromatography. The method is based on the non-fluorescence of non-fluoranthenic hydrocarbons and the fluorescence of fluoranthenic hydrocarbons in nitromethane solution. By this technique the two types of compound can be differentiated on a thin-layer plate or in solution.

Zusammenfassung—In dieser Arbeit, die die erste einer Reihe weiterer Arbeiten sein soll, wird eine neue Art der Analyse fluoreszierender Moleküle eingeführt: die Fluoreszenz-Löschungs-Analyse. Diese Methode wird in der organischen Spurenanalyse einen weit verzweigten Anwendungsbereich finden. Es wird dabei analytischer Gebrauch von dem Effekt der Fluoreszenzlöschung gemacht. Verbindungen wie Anthracen, Phenanthren, Pyren, Benz(*a*)anthracen, Benzo(*a*)pyren, Perylen usw. fluoreszieren in Nitromethanlösung nicht, während Kohlenwasserstoffe mit Fluoranthenring fluoreszieren. Diese Erscheinung wurde dazu ausgenutzt, Fluoranthen und Benzo(*k*)fluoranthen in Schwebeteilchen aus der Luft nach vorhergegangener Säulenchromatographie zu identifizieren. Die Erscheinung wurde auch bei der Dünnschichtchromatographie direkt auf der Platte ausgenutzt.

Résumé—Dans ce premier mémoire d'une série, on présente une nouvelle méthode analytique pour l'analyse des molécules fluorescentes: l'analyse par extinction de fluorescence. Ce domaine de recherches aura des ramifications lointaines dans l'analyse organique de traces. On utilise analytiquement l'effet d'extinction en spectrophotofluorimétrie. On a trouvé que des composés tels que l'anthracène, le phénanthrène, le pyrène, le benzo(*a*)anthracène, le benzo(*a*)pyrène, le pérylène, etc. ne sont pas fluorescents en solution dans le nitrométhane, cependant que des hydrocarbures contenant le noyau fluoranthénique sont fluorescents. On a utilisé ce phénomène en caractérisant le fluoranthène et le benzo(*k*)fluoranthène dans les particules en suspension dans l'air, après chromatographie sur colonne. Le phénomène a été également utilisé en chromatographie sur couches minces, directement sur la plaque.

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SOME RATHER UNUSUAL CHEMICAL ANALYSES

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Summary—Some rather unusual chemical analyses are described. A typical example is the determination of a few μg of one element in a sample composed essentially of the elements listed in the periodic table. This somewhat bizarre sample is a solution containing 10 mg each of about seventy different elements.

INTRODUCTION

FOR the past few years, the authors and their colleagues have been concerned with developing methods for the determination of trace elements in beryllium and beryllium oxide.¹⁻⁷ Although these methods were developed primarily for application to a beryllium matrix, they were intended to have much wider usage.

It is the authors' opinion that the determination of a trace amount of an element in a matrix is rarely difficult because of the particular matrix. The real difficulty is the presence in the matrix of unknown amounts of other elements which can interfere with the method to be used. A check of the analytical literature will immediately reveal that few indeed are the methods which have been investigated comprehensively. Rarely does one know which elements of all those in the periodic table interfere, and in what amounts. Consequently, the analyst must frequently use a method whose limitations are unknown, and must apply it to a sample which might contain a number of interfering elements. Therefore, we attempted to develop, within certain limitations, specific methods of analysis. Although many tests of these methods have been made, the most critical test made is the one here described.

When measuring the effect of other elements in an analytical procedure, it is common practice to test the effect of each individual element on the determination of the constituent, in this case a trace element. However, "other elements" do not occur individually in a sample, but rather in an assorted collection of kinds and amounts. Furthermore, if there are n elements to be included in the investigation, there would be $2^n - 1$ combinations to be tested. This assumes that all elements would be at the same concentration level. Because the latter situation is never true, one can easily see that there is an infinite number of combinations to test. In order to make a meaningful test of the effect of other elements, it is necessary to simplify this situation. The method chosen was to measure the effect, if any, of all elements added simultaneously at one concentration level—10 mg.

The effect of 71 elements was tested (72 minus the element being determined): aluminium, antimony(III), arsenic(III), barium, beryllium, bismuth, boron, bromine (as bromide), cadmium, calcium, cerium(IV), caesium, chlorine (as chloride), chromium(III), cobalt, copper, dysprosium, erbium, europium, fluorine (as fluoride), gadolinium, gallium, germanium(IV), gold, hafnium, holmium, indium, iodine (as iodide), iridium, iron, lanthanum, lead, lithium, lutetium, magnesium, manganese(II), mercury(II), molybdenum(VI), neodymium, nickel, niobium, palladium, phosphorus (as phosphate), platinum, potassium, praseodymium, rhenium(VII), rhodium, rubidium, samarium, scandium, selenium, silicon (as silicate), silver, sodium, strontium, sulphur (as sulphate), tantalum, tellurium(IV), terbium, thallium(I), thorium, thulium, tin(II), titanium, tungsten, uranium(VI), vanadium(V), ytterbium, yttrium, zinc and zirconium. It should be noted that two valence states of an element were used for several of the tests.

All of the above elements were added (in the valence state indicated) in every test, except where noted.

The technique used to make the test was as follows. Fifty mg of each of the elements (in solution) were added to a beaker, together with the appropriate amounts of acid(s) and complexing agent, if any. If precipitation or hydrolysis occurred, the solution was filtered and the precipitate was analysed to determine what amounts of what elements were not being included in the test. This analysis is given under *Analysis of Residue*. The filtrate was then diluted to a convenient volume and divided into 5 equal parts. One part was used to make an estimate of the amount of the element being determined which was present as a trace in the elements added. Two parts, labelled B1 and B2, were carried through the procedure as blanks. In order to confirm the fact that the absorbance of the blank was caused by the element being determined, the coloured solution was analysed spectrographically. Although this measurement may not be very accurate, it is sufficiently so to confirm the fact that the absorbance measured was actually caused by the element being determined. This spectrographic analysis is listed under *Element found, spectrographic*.

The other two parts of the solution, labelled S1 and S2, were "spiked" with an appropriate amount of the element being determined and analysed by the method developed for this particular element.

EXPERIMENTAL * AND RESULTS

Determination of iron¹

Eight hundred ml of a solution were obtained containing the elements whose effect was to be investigated. Titanium was added as Ti^{III}. Silicon was not added because of its tendency to form an emulsion during extraction. Tellurium, gallium, and uranium were not added because of their known interference effect. The solution, 6M with respect to hydrochloric acid, containing 5 g of citric acid and sufficient bromine to oxidise the iron, was divided as described and treated as follows.

Six extractions were made with 25 ml of 0.01M tri-n-octylphosphine oxide (TOPO) in cyclohexane. The combined extracts were shaken with 35 ml, 35 ml and 10 ml of 3M sulphuric acid (iron reverted to the aqueous phase). The sulphuric acid phase was washed 10 times with 25-ml portions of 0.1M TOPO in chloroform and the organic phases were discarded. Sixty ml of hydrochloric acid were added, and the iron was extracted with 10 ml of 0.01M TOPO in cyclohexane. A 1-ml aliquot was transferred to a 25-ml volumetric flask containing 15 ml of isopropyl alcohol and sufficient hydroquinone for reduction of the iron. After addition of 1,10-phenanthroline, iron was determined as the iron(II)-phenanthroline complex. The results are shown in Table I.

* Because of the number of methods discussed, the reader is referred to the original publications for greater detail concerning reagents, procedures, etc.

The results indicate that accurate results will be obtained using this method if:

- (1) the amount of silicon is reduced to a level at which it will not cause emulsification when the TOPO extraction is made;
- (2) sufficient initial extractions are made to remove iron;
- (3) the 1,10-phenanthroline complex solution is clear when the final absorbance measurement is made;
- and (4) gallium, tellurium and uranium are below the level indicated in the published report.

TABLE I.—TEST OF IRON METHOD

Soln.	Iron, μg		Recovery %	Iron found (spectrographic) μg
	Added	Found		
B1	—	66.2	—	90
B2	—	71.7	—	—
S1	103.5	170	98	—
S2	103.5	171	98	—

Analysis of residue (on the basis of 10 mg added): 10 mg of Ba, 4 mg of Hf, 2 mg of Ta, and 1.5 mg of Zr.

Determination of copper^a

Twelve hundred ml of a solution were obtained containing the elements whose effect was to be investigated. Iron was added as both Fe^{II} and Fe^{III} (50 mg of each), manganese as both Mn^{II} and Mn^{VII} (50 mg of each), and titanium as both Ti^{III} and Ti^{IV} (50 mg of each). Chromium and hafnium were not added. The solution, which contained 25 g of citric acid, 25 ml of hydrochloric acid, 50 ml of sulphuric acid and 5 g of hydroxylamine hydrochloride (to reduce the copper), was neutralised to a pH of 5.0, and divided as described.

Copper was determined by extraction of the neocuproine complex using the method described^a except that the extraction was made with 25 ml of 4-methyl-2-pentanone, and the absorbance was measured using 2-cm cells. The results are shown in Table II under B1 and S1. When the extracts were diluted in a volumetric flask (because of the varying solubility of 4-methyl-2-pentanone in the aqueous phase) the results were somewhat better, as shown by B2 and S2 in Table II.

TABLE II.—TEST OF COPPER METHOD

Soln.	Copper, μg		Recovery, %	Copper found (spectrographic) μg
	Added	Found		
B1	—	14.6	—	15
S1	60.9	72.2	95	—
B2	—	16.5	—	15
S2	60.9	77.4	100	—

Analysis of residue (on the basis of 10 mg added): 10 mg of Ba, 4 mg of Au, 4 mg of Pt, 4 mg of Sr, 1.6 mg of Rh, and 1.6 mg of Pb.

When the same experiment was performed in the presence of 10 mg each of Cr^{III}, Cr^{VI} and Hf, only 90% recovery of the added copper was obtained, in agreement with the published report (*loc. cit.*).

Determination of molybdenum^a

In addition to the elements whose effect was to be investigated, the solutions to be analysed contained the proper amounts of tartaric acid, hydrochloric acid and sulphuric acid. Barium, gold, and silver were not added because of the tendency of the large amount of precipitate to clog the separatory funnel. Palladium, platinum, rhenium, selenium and tellurium were not added because of their known interference effect. Molybdenum was extracted as the thiocyanate complex with 4-methyl-2-pentanone. The results are shown in Table III.

TABLE III.—TEST OF MOLYBDENUM METHOD

Soln.	Molybdenum, μg		Recovery, %	Molybdenum found (spectrographic) μg
	Added	Found		
B1	—	5.6	—	5
B2	—	5.6	—	5
S1	75	78.7	97	—
S2	75	78.7	97	—

Determination of cobalt⁴

In addition to the elements whose effect was to be investigated, the solutions to be analysed contained the proper amounts of hydrochloric acid, sulphuric acid and citric acid. Iron was added as both Fe^{II} and Fe^{III} (50 mg of each), and titanium as Ti^{III} and Ti^{IV} (50 mg of each). Chromium and manganese were not added in order to omit an ion-exchange step.

After adjustment of the pH to 4.0, the solutions were washed several times with acetylacetone. Sodium thiocyanate was added and cobalt was extracted as the thiocyanate complex with acetylacetone. The results are shown in Table IV.

TABLE IV.—TEST OF COBALT METHOD

Soln.	Cobalt, μg		Recovery, %	Cobalt found (spectrographic) μg
	Added	Found		
B1	—	5	—	4
B2	—	5	—	4
S1	106	108	97	—
S2	106	108	97	—

Analysis of residue (on the basis of 10 mg added): 10 mg of Ba, 10 mg of Ag, 1.6 mg of Sr, 1.2 mg of Zr, 0.8 mg of Pd, and 0.8 mg of Rh.

Determination of cadmium^{5}*

In addition to the elements whose effect was to be investigated, the solution contained the proper amounts of hydrochloric, sulphuric and citric acids. Iron was added as Fe^{III} , and titanium as Ti^{III} . Cadmium was precipitated from an ammoniacal citrate solution with benzotriazole using nickel as a collector. After treatment of the precipitate with nitric and perchloric acids, a 10% hydrochloric acid solution of the residue was passed through an anion-exchange column. Cadmium, retained by the resin and subsequently eluted with 3M nitric acid, was finally determined by extraction from a strongly alkaline medium with a chloroform solution of dithizone. The results are shown in Table V.

TABLE V.—TEST OF CADMIUM METHOD

Soln.	Cadmium, μg		Recovery, %	Cadmium found (spectrographic) μg
	Added	Found		
B1	—	1.1	—	1
B2	—	1.3	—	—
S1	3	4.2	100	—
S2	5	6.0	96	—

Determination of niobium and tantalum^{6}*

In addition to the elements to be investigated, the solution contained the proper amounts of sulphuric acid and hydrochloric acid. Titanium was not added. Niobium and tantalum were precipitated with cupferron using zirconium as a collector. After ignition of the precipitate and fusion with sodium bisulphate, the fused mass was dissolved in 25% hydrochloric acid-20% hydrofluoric acid and added to an anion-exchange column. Niobium and tantalum were eluted from the column separately, and again precipitated with cupferron as before. After fusion and dissolution of the precipitates, niobium was determined as the hydroquinone complex and tantalum as the pyrogallol complex. The results are shown in Tables VIA and VIB.

* Test made at Ledoux and Company by S. Kallmann *et al.*

TABLE VIA.—TEST OF NIOBIUM METHOD

Soln.	Niobium, μg		Recovery, %	Niobium found (spectrographic) μg
	Added	Found		
B1	—	142	—	—
B2	—	153	—	130
S1	700	805	94	—
S2	1400	1490	96	—

Analysis of residue (on the basis of 10 mg added): 10 mg of Ba, 10 mg of Ag, 10 mg of Sr, 10 mg of P, 2 mg of Au, 1.5 mg of Pd, 0.5 mg of Zr, 0.5 mg of Hf, and 0.5 mg of Pb.

Niobium and tantalum were determined in the same solution; consequently, the *Analysis of residue* in Table VIA applies to Table VIB also. When titanium was added with the rest of the elements, the results were high and erratic. Titanium was not completely removed from the ion-exchange column, despite the fact that it does not interfere with the determination of niobium and tantalum when it (titanium) is added by itself. This is the first indication of a "synergistic effect" in any of the methods thus far.

TABLE VIB.—TEST OF TANTALUM METHOD

Soln.	Tantalum, μg		Recovery, %	Tantalum found (spectrographic) μg
	Added	Found		
B1	—	43	—	—
B2	—	47	—	a
S1	819	877	102	—
S2	1638	1708	102	—

a Not detected spectrographically.

Determination of nickel⁷

In addition to the elements to be investigated, the solution contained the proper amounts of sulphuric acid, hydrochloric acid, and tartaric acid. Titanium was added both as Ti^{III} and Ti^{IV} (50 mg of each), and chromium was added both as Cr^{III} and Cr^{VI} (50 mg of each). Nickel was precipitated from an ammoniacal citrate solution with benzotriazole using cadmium as a collector. After treatment of the precipitate with nitric and perchloric acids, the residue was dissolved in a mixture of hydrochloric acid and isopropyl alcohol, and an anion-exchange separation was performed. Nickel was finally determined as the aqueous dimethylglyoxime complex. The results are shown in Table VII.

TABLE VII.—TEST OF NICKEL METHOD

Soln.	Nickel, μg		Recovery, %	Nickel found (spectrographic) μg
	Added	Found		
B1	—	68.0	—	55
B2	—	68.3	—	54
S1	100	167.5	99	—
S2	100	166.5	98	—

Analysis of residue (on the basis of 10 mg added): 10 mg of Ag, 10 mg of Au, 7.5 mg of Ba, 2.5 mg of In, 0.5 mg of Sr, and 2 mg of rare earths.

DISCUSSION

At one time it was hoped that the analyst's shelf would some day consist of a reagent specific for the determination of each element. Today, this idea seems to be somewhat naïve, although it may yet come to pass. However, the analyses presented here seem to indicate that specific methods can be developed. Furthermore, it is very

evident that these methods are practical; *i.e.*, they can be applied to a wide variety of samples. The application of these methods will be the subject of a forthcoming paper.

It should be of interest at this time to repeat (but not in their original order) some of the remarks made by Lundell.⁸

. . . there is an increasing tendency to devote more and more time to determinations which deal with the final act of a chemical analysis, and less time to chemical analysis itself—in other words, to consider chemical analysis as dealing with one or two variables instead of the dozen or more that are often involved. . . . Of course, there is good reason for confining analytical discussions to determinations which involve one or two variables. A system containing ten to twenty diverse components can hardly be handled on a strictly scientific basis, and any handling of it requires actual experience in analysis. . . . Methods of the type described (methods dealing with one or two variables) are about as helpful to the analyst as the method for catching a bird which the old folk used to recommend to children—namely to sprinkle salt on its tail. To do that one obviously must have the bird in hand, and in that case there is no need for the salt. . . . There is no dearth of methods that are entirely satisfactory for the determination of elements when they occur alone. The rub comes in because elements never occur alone, for nature and man both frown on celibacy. Methods of determination must therefore be judged by their “selectiveness.” It is in this respect that most methods are weak and that improvements must come. . . . Because of their lack of selectivity, methods for the chemical analysis of things as they are do not stay put. Therein lies the danger of standard methods of analysis. As soon as the other group members creep in—for example, through changes in manufacture—the method must be changed.

These remarks, made over thirty years ago, are still appropriate today, with, we think, but one exception. It has been our endeavour to develop standard methods of analysis (which, of course, can be replaced or improved as new advances are made). The results of this paper indicate that specific methods can be developed, and the forthcoming paper will indicate the wide applicability of such methods.

In conclusion, it is the authors' opinion that these analyses are unique in the field of chemical analysis and should arouse the interest and thoughtful speculation of today's Lundells.

Acknowledgement.—The authors gratefully acknowledge those individuals who assisted in the development of these methods. The authors are greatly indebted to Dr. Louis Gordon who suggested this particular test.

Zusammenfassung—Enige ziemlich ungewöhnliche chemische Analysen werden beschrieben. Ein typisches Beispiel ist die Bestimmung weniger Mikrogramme eines Elements in einer Probe, die fast alle Elemente des periodischen Systems enthält. Es handelt sich um eine Lösung, die je 10 mg von etwa 70 verschiedenen Elementen enthält.

Résumé—On décrit quelques analyses chimiques un peu inhabituelles. Un exemple typique en est le dosage de quelques microgrammes d'un élément dans un échantillon essentiellement composé des éléments figurant dans le tableau périodique. Cet échantillon quelque peu bizarre est une solution contenant 10 mg de chacun d'environ soixante-dix éléments différents.

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STUDIES OF THE FIRE ASSAY FOR PLATINUM METALS BY LEAD COLLECTION

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Summary—A fire-assay procedure for determining platinum, palladium, rhodium or iridium in the nitric acid parting solution from a lead button is described. Palladium is the only metal which is completely attacked by the parting solution; traces of platinum and rhodium are also dissolved. The presence of copper in the lead button has been found to encourage the dissolution of both platinum and iridium in the nitric acid parting solution; rhodium remains unaffected. Ion-exchange and precipitation procedures for separating palladium from lead are also included. Efforts have been made to identify the source of iridium loss which is a characteristic of classical fire assay collections.

FUNDAMENTALLY, there are two stages to the classical fire assay collection of the noble metals. The initial stage involves the accumulation by lead of the noble metals from the fusion flux prepared to provide the lead *in situ*. The result is a lead alloy containing the noble metals, called a button or regulus. The second stage involves the removal of lead from the button by volatilisation of litharge and its absorption by a cupel to form, finally, a silver alloy. A variation of this approach is a cupellation to accomplish the so-called dry assay, which is made in the absence of added silver. Traditionally, the formation of the silver alloy is followed by a series of wet separations whose character depends upon the composition of the silver collecting medium.

In recent years, the efficiency of the recovery by the silver alloy has been examined critically. In the case of iridium, it has become evident that a loss may result from mechanical processes, partly because iridium appears as intrusions on the surface of the silver bead.¹ The same phenomenon is observed with rhodium and ruthenium, except that with the latter two metals the loss is relatively small. In any case, with these three metals, there is always a considerable risk of loss except when the metals are present in microgram quantities. In the case of osmium the cupellation process can result in a complete disintegration of the silver bead, sometimes explosively. Undoubtedly this is caused by the expulsion of the readily formed volatile octavalent oxide formed with the oxygen, which is significantly soluble in silver at cupellation temperatures. On the other hand, gold, platinum and palladium silver beads can be produced and the noble metals subsequently separated by wet methods with accuracy and simplicity. In addition to the probability of cupellation losses of the more insoluble platinum metals, the subsequent wet treatments involved in separations and determinations of these metals require a high order of analytical skill.

Thus, while one must acknowledge the superiority of the cupellation process for the more common noble metals, one may hope for a more efficient method for the determination of osmium, ruthenium, iridium and rhodium immediately following

a collection by lead. Recent researches with these four metals have provided evidence that the lead collection stage of the assay provides for a complete recovery of osmium and ruthenium.² Proof for this has been obtained by the use of perchloric acid, as a parting acid for the lead button, and simultaneously as an oxidant to form the octavalent oxides of both osmium and ruthenium. Information has also been provided to indicate a satisfactory recovery of rhodium.³

Because of the deficiencies of recovery of the more insoluble noble metals by cupellation to form the silver bead, and the inherent problems associated with their wet treatment, and because the lead alloy has proved to be an effective collector for the noble metals with the possible exception of iridium, it seemed profitable to examine the possibility of a wet analysis of the button, thus obviating the necessity of a cupellation.

Any effort to provide ultimately a complete wet procedure for the determination of noble metals in lead-assay buttons required first a preliminary examination of the composition of the nitric acid parting solution. The few recorded procedures for the analysis of the lead button, none of which is either proved or recorded in detail, were based on the assumption that of the noble metals, palladium was the only metal simultaneously attacked by the nitric acid parting solution. The restricted classical procedure involves the precipitation and filtration of lead sulphate, and the removal of adsorbed palladium by dissolution in ammonium acetate and reprecipitation as the sulphate. Undoubtedly, it is this cumbersome and inaccurate method which has discouraged attempts to provide complete and accurate procedures for the analysis of the lead button.

A direct lead-fusion method for the analysis of platinum-iridium alloys was developed by Gilchrist.⁴ By this method the button was parted with nitric acid, and the residue was treated with *aqua regia*; iridium in the residue was determined gravimetrically. The results obtained suggest that iridium is not attacked by the parting acid used, and the small observed loss is probably the result of a slight dissolution of iridium in *aqua regia*. However, the lead button obtained by normal assay procedures differs from that obtained by Gilchrist in that appreciable amounts of copper and other base metals are often present. The influence of copper and other base metals on the dissolution of platinum metals by the nitric acid parting solution has not been recorded, although it is known that traces of copper will encourage the dissolution of precipitated platinum when the latter is leached with nitric acid.

Various techniques were applied by the present authors to determine the platinum metals content of the nitric acid solution used to part the button. The selective precipitation and ion-exchange methods described below proved of limited value. Although acceptable separations and determinations of the palladium in the parting acid could be made in the presence of other platinum metals, the techniques proved cumbersome and inaccurate. However, it seemed reasonable that an evaporation of the lead-nitric acid parting solution and a subsequent roasting to form litharge, together with the addition of flour and the usual fluxing constituents, followed by a fire assay would prove to be an applicable technique.

The fire-assay treatment described below was applied to nitric acid parting solutions derived from the dissolution of lead buttons. Initial determinations with buttons containing palladium, platinum, rhodium and iridium indicated that the parting acid contained high proportions of palladium and traces of rhodium and platinum. In

the case of iridium, dissolution occurred only when copper was present in the button. Evidence was also obtained to indicate that the presence of copper in the lead button encouraged the dissolution of platinum. Because copper is a natural associate of the platinum metals, and frequently appears in small amounts in lead-assay buttons, it was necessary to determine its influence on the codissolution of the platinum metals. Methods described below allowed for the determination of each of the four platinum metals in a nitric acid parting solution. In the event that the amounts of platinum, rhodium and iridium in the parting acid are not considered significant, and a palladium separation only is required, the precipitation and ion-exchange procedures described below may also be applied.

EXPERIMENTAL

Standard solutions

Platinum: Pure platinum sponge was dissolved by *aqua regia*, and the nitric oxides were removed by repeated evaporation with hydrochloric acid. The platinum content was determined gravimetrically by thiophenol. The solution contained 1.011 mg of platinum per ml.

Palladium: Palladium chloride was dissolved in water with the addition of a little hydrochloric acid. Precipitation by the sodium salt of dimethylglyoxime yielded 0.994 mg of palladium per ml.

Rhodium: Sodium rhodium chloride was dissolved in water and standardised gravimetrically by 2-thiobarbituric acid. The solution contained 0.958 mg of rhodium per ml.

Iridium: Ammonium chloro-iridate was dissolved in water and standardised gravimetrically by 2-mercaptobenzthiazole. The solution contained 1.042 mg of iridium per ml.

The chemicals used were all of C.P. reagent grade.

Apparatus

Assay crucibles, 30-g, were supplied by A. P. Green Fire Brick Co. Ltd., Canada. The furnace used was a Williams and Wilson, 25 cycle-15 kV-amp. Globar type. For colorimetric measurements a Beckmann model B spectrophotometer was used with 10-mm glass cells.

Procedure

The following three fusion mixtures were used:

A	
Litharge	125.3 g
Sodium carbonate	30.0 g
Silica	21.7 g
Flour	1.0 g
B	
Litharge	124.2 g
Copper oxide	1.5 g
Sodium carbonate	30.0 g
Silica	21.9 g
Flour	1.0 g
C	
Litharge	122.5 g
Copper oxide	3.0 g
Sodium carbonate	30.0 g
Silica	22.7 g
Flour	1.0 g

In each case three buttons and one blank button were prepared.

About two-thirds of the fusion mixture was transferred to a porcelain dish previously lined with an 8-in.² Cellophane sheet. A small depression was made at the centre of the dish, and the mixture was salted with 5.0 ml of the standard solution (1.0 ml in the case of platinum). The mixture was dried overnight in an air oven at 70°, then 10 g of fusion mixture were carefully transferred to a 30-g assay crucible previously lined with an 8-in.² Cellophane sheet. The remaining fusion mixture was added to the material in the crucible.

The crucible was transferred to the furnace at a temperature of about 1150°. The temperature was raised to 1225° over a period of 35–40 min, at which time the fusion was considered to be

complete. The fused mixture was then transferred to a conical iron mould, from which a clean lead button was obtained on cooling.

Assay of the slag: The slag was crushed, pulverised to a fineness of 45-mesh and mixed with 27 g of litharge, 3 g of flour and 20 mg of silver powder. The mixture was transferred to the original assay crucible and assayed. The lead button obtained was cupelled to the silver bead, which was treated in the same manner as that obtained from the assay of the parting solution, except in the case of palladium.

Parting of the button: The button was treated with nitric acid (1:2 in case of palladium and 1:4 for other metals) and parted on a hot water bath. Subsequent to the dissolution of the button, 100 ml of water were added and the residue was allowed to settle. The latter was filtered, washed and treated as described below for the individual metals.

Treatment of the parting solution: The parting solution, including the washings, was evaporated to dryness on a hot water bath and the dried material was transferred to an assay crucible. The beaker in which the evaporation was made was washed with dilute nitric acid, and the washings were evaporated to dryness. This residue was also added to the assay crucible, and the mixture was heated for 1.5 hr in an electric furnace maintained at 750°, by which time the decomposition of lead nitrate to lead oxide was complete. The crucible was cooled, and the lead oxide was removed and weighed. Accepting this weight of the lead oxide as the weight of the sample, the required quantity of a monosilicate flux of the type $2\text{Na}_2\text{O} \cdot \text{SiO}_2$ was prepared and mixed with the lead oxide. It has been found that a monosilicate flux of this type can be used effectively for collecting platinum and palladium along with traces of rhodium and iridium.⁵

The following typical flux composition was used: weight of lead oxide obtained = 30.1 g; sodium carbonate = 30.1 g; silica = 14.0 g; litharge = 27.0 g; flour = 3.0 g; silver = 20 mg.

The fusion mixture was transferred to the same assay crucible used for the conversion of lead nitrate to lead oxide, and was heated at 1150° for 35–40 min. The cleaned lead button was cupelled at 1000° to obtain a silver bead. The bead method was used here because it was expected, and later proved, that, of the platinum metals, only palladium would be present in appreciable proportion; platinum, rhodium and iridium would be present only in microgram quantities, in which case the silver bead method, as described earlier, could be applied successfully. The bead was parted with 1:2 nitric acid, and the residue was filtered, washed and ignited. The ignited residue in the case of platinum and palladium was dissolved in *aqua regia*, and in the case of rhodium and iridium by chlorination in the presence of sodium chloride. Silver was precipitated as chloride from the filtrate obtained

TABLE I. RECOVERY OF PLATINUM BY LEAD FIRE ASSAY

Flux no.	Weight of button, g	Platinum in residue from parting acid, mg	Platinum in parting solution, mg	Platinum found in slag, mg	Total platinum recovered, mg	Platinum added, mg	Recovery, %
A	27.6	0.918	0.034	0.003	0.955	1.011	94.6
	29.8	0.944	0.031	0.003	0.978	1.011	96.5
	28.0	0.939	0.029	0.008	0.976	1.011	96.5
B	30.0	0.815	0.153	0.004	0.972	1.011	96.2
	30.2	0.801	0.156	0.005	0.962	1.011	95.2
	25.7	0.806	0.150	0.005	0.961	1.011	95.1

after dissolving the silver bead; any adsorbed platinum metal was removed by dissolving the precipitate in aqueous ammonia and reprecipitating the silver chloride. The solutions were mixed, and the platinum metals were determined either gravimetrically or colorimetrically as described below.

Fire-assay recovery of platinum, palladium, rhodium and iridium

Lead buttons were obtained after the fusion of the fluxes A, B and C, previously salted with standard solutions of the platinum metals, and were parted with nitric acid as described above.

Platinum: The parting residue containing platinum was ignited at 600° and dissolved in *aqua regia*. The oxides of nitrogen were removed by repeated evaporation with hydrochloric acid in the presence of 4 drops of 2% sodium chloride solution. Platinum was determined colorimetrically by stannous chloride reagent.

The parting solution was assayed as described above, and platinum was determined in the silver beads colorimetrically.

In the absence of base metals, Hoffman and Beamish⁶ used a nitre method, and reported a recovery of 97.3% of platinum.

Palladium: After treatment of the parting residue with *aqua regia* and then with hydrochloric acid, palladium was determined colorimetrically by *p*-nitrosodiphenylamine.

The palladium in the silver bead obtained from the parting solution was determined gravimetrically by the sodium salt of dimethylglyoxime, but in the silver bead obtained from the slag palladium was determined colorimetrically as above.

TABLE II. RECOVERY OF PALLADIUM BY LEAD FIRE ASSAY

Flux no.	Weight of button, g	Palladium in residue from parting acid, mg	Palladium in parting solution, mg	Palladium found in slag, mg	Total palladium recovered, mg	Palladium added, mg	Recovery, %
A	31.5	0.009	4.75	0.124	4.883	4.97	98.2
	30.0	0.009	4.75	0.110	4.869	4.97	98.0
	30.8	0.008	4.67	0.109	4.787	4.97	96.3
B	29.2	0.007	4.69	0.132	4.829	4.97	97.2
	27.4	0.007	4.69	0.138	4.835	4.97	97.3
	28.4	0.007	4.77	0.129	4.906	4.97	98.7

With a fusion mixture of the same silicate degree, but carrying out the analysis by a different method, Fraser and Beamish⁷ reported an average recovery of 97.4% of palladium in the absence of added base metals.

Rhodium: The residue obtained after parting a lead button as described for platinum was ignited at 850° for 20 min, cooled, hydrogenated for 15 min, and then chlorinated at 600° for 8 hr in the presence of about 50 mg of sodium chloride. Rhodium was determined gravimetrically by 2-thio-barbituric acid.

Rhodium in the silver beads obtained from the parting solution and the slag was brought into a soluble form by chlorination as described above and then determined colorimetrically by stannous bromide.

TABLE III. RECOVERY OF RHODIUM BY LEAD FIRE ASSAY

Flux no.	Weight of button, g	Rhodium in residue from parting acid, mg	Rhodium from parting solution, mg	Rhodium found in slag, mg	Total rhodium recovered, mg	Rhodium added, mg	Recovery, %
A	31.2	3.32	0.820	0.010	4.150	4.79	86.6
	30.7	3.33	0.836	0.025	4.191	4.79	87.5
	32.6	3.57	0.740	0.015	4.325	4.79	90.3
B	27.4	3.96	0.579	0.031	4.570	4.79	95.4
	30.2	3.61	0.885	0.008	4.503	4.79	94.0
	29.9	3.78	0.754	0.019	4.553	4.79	95.1

In the absence of base metals, Allen and Beamish⁸ have reported an average recovery of 96% of rhodium from the synthetic lead-rhodium buttons.

Iridium: The residue obtained from the parting acid in the case of iridium-lead buttons was ignited at 650° for 45 min, cooled, hydrogenated for 1 hr, and then chlorinated for 8 hr as in the case of rhodium. Iridium was obtained in soluble form and was determined gravimetrically by 2-mercaptobenzthiazole.

The lead button obtained from the parting solution was not cupelled directly, but was treated as in the case of the original button. This variation was introduced because, as noted earlier, cupellation losses of iridium are significant if the lead button contains a large amount of iridium. The parting solution obtained after parting this second button was subjected to a treatment similar to that in the case of platinum, palladium or rhodium, *e.g.*, the lead button was cupelled and then the iridium in the silver bead was determined colorimetrically by stannous bromide.

Barefoot and Beamish,⁸ working with acidic fluxes, reported an average recovery of iridium of the order of 99%. Presumably the percentage recovery in the present instance is low because of the more basic fluxes used; these fluxes were used here because of their greater efficiency for platinum metals in general. With a mono-silicate flux, Barefoot and Beamish⁸ found a recovery of 96% of iridium with a 0.5-mg sample of iridium.

Influence of copper on the dissolution of platinum metals in nitric acid

As stated above the lead buttons obtained from a fusion of ores from the natural deposits of the platinum metals frequently carry traces of copper. It was observed in preliminary experiments that

TABLE IV. RECOVERY OF IRIIDIUM BY LEAD FIRE ASSAY

Flux no.	Weight of button, g	Iridium in residue from parting acid, mg	Iridium from parting solution, mg	Iridium found in slag, mg	Total iridium recovered, mg	Iridium added, mg	Recovery, %
A	29.4	4.98	nil	nil	4.98	5.21	95.6
	28.9	4.97	nil	nil	4.97	5.21	95.4
	31.1	4.97	nil	nil	4.97	5.21	95.4
B	28.5	3.39	1.15	nil	4.54	5.21	87.2
	28.7	3.47	1.00	nil	4.47	5.21	85.8
	30.2	4.28	0.249	nil	4.529	5.21	86.9
C	27.9	2.61	1.14	nil	3.75	5.21	72.0
	28.6	2.81	1.43	nil	4.24	5.21	81.4
	29.9	2.35	1.36	nil	3.71	5.21	71.2

the presence of copper in the lead button affects the distribution of the platinum metals between the parting acid and the acid insoluble. Other researches on platinum, palladium, rhodium and iridium clearly indicate that the total recovery of these precious metals by lead fire-assay collection is affected by the presence of copper in the flux or in the lead button.^{3,6-8} In order to determine the influence of copper on the extent of dissolution of the platinum metals, lead buttons were prepared to contain various amounts of copper. These were parted with nitric acid, and the quantity of the platinum metal in the parting solution was determined by the procedure described above. The results are recorded in Table V.

TABLE V. INFLUENCE OF COPPER ON THE DISSOLUTION OF PLATINUM, PALLADIUM, RHODIUM AND IRIIDIUM IN NITRIC ACID

Amount of copper in button, g	Average quantity of noble metal found in the parting solution			
	Platinum, mg	Palladium, mg	Rhodium, mg	Iridium, mg
nil	0.031	4.72	0.799	nil
0.35	0.153	4.68	0.739	0.800
0.68				1.310

The above results indicate that the amount of platinum and iridium in the parting solution increases with an increase of copper in the button. In preliminary experiments, it was observed also that if 5 mg of iridium are collected in pure copper, and the button is parted with nitric acid, the dissolution of iridium is practically complete.

Losses of iridium in a fire assay

It may be noted from the above results that the recovery of iridium by the lead-collection method may be adversely affected by the presence of copper in the slag. Barefoot and Beamish reported that the recovery of iridium is low in the presence of both nickel and copper. Iron may, however, be tolerated. Although the sources of the loss of iridium have not been determined, it has been assumed that the losses occur to the slag or to the pot wall.

Losses to the slag

Barefoot and Beamish⁸ observed that after the initial fusion the recovery by lead from the slag was not efficient, even after a number of re-assays. However, a spectrographic examination of the monosilicate and basic slags failed to show the presence of iridium.

In the present investigation an attempt was made to determine the losses to the slag by neutron activation. The procedure employed was as follows.

Representative samples (about 60 mg each) of the ground slag were wrapped in aluminium foil and subjected to neutron bombardment. After the activation was complete, the hot samples were left for 2–3 weeks to allow the decay of radioactive sodium. The samples were transferred to plastic containers, the intensities were measured in the different energy channels, and were compared with those of the blank slag salted with known amounts of iridium (about 0.1 μg). No significant amount of iridium was found to be present in the slag.

Losses to the pot wall

For the fusion of the pot wall, a basic flux is required, *i.e.*, a ratio of acid oxygen to basic oxygen of the order of 0.5. The 30-g assay crucible, in which the fire-assay collection for iridium was carried out by using flux (B) or (C), was crushed and pulverised to a fineness of 45-mesh and mixed with the following flux:

Weight of pot wall taken	=	60 g
Sodium carbonate	=	60 g
Calcium oxide	=	37.5 g
Silica	=	12.5 g
Borax	=	12.5 g
Litharge	=	154.0 g
Flour	=	4.3 g
Silver	=	20 mg

The assay was made at 1200° for 1.5–2 hr, producing a clear and homogeneous slag. The lead buttons were cupelled to obtain silver beads, which were subsequently analysed for iridium colorimetrically by the stannous bromide method.

No detectable amount of iridium was recovered from the pot wall.

A standard solution containing 1.04 mg of iridium was added to the inside walls of a new 30-g assay crucible, the crucible was then dried overnight in an air oven and subjected to the same treatment as above; the weight of iridium recovered was 0.177 mg.

It would seem that the fusion process results in some incorporation of iridium with the pot wall. Because assay pots are essentially silicates, a basic flux is required for a suitable fusion. Fluxes of this type are ineffective for the quantitative collection of iridium.⁸ In any case, the sources of loss of iridium during a fire assay have not yet been determined, although by process of elimination it is not unlikely that some inclusion with the pot wall does occur.

Separation and determination of palladium in the presence of lead

By the above assay procedure evidence was obtained to indicate the presence of large amounts of palladium and only traces of platinum and rhodium in the nitric acid parting solution. In general assay practice, and particularly in those instances where assay results are obtained for the purpose of indicating the commercial value of a natural deposit, the content of platinum, palladium and gold is of primary importance, and the small traces of platinum present in the parting solution are of relatively little significance. In these instances an effective method of isolating the palladium in the parting acid is useful. Efforts were made to provide a procedure which would avoid the necessity of the cumbersome lead sulphate separation.

Ion exchange

Recently, ion-exchange procedures for the isolation of platinum metals from large amounts of base metals, such as iron, copper and nickel, have been reported.⁵ The methods involve the conversion of the six platinum metals to stable anionic halides and the base metals to a cationic form. Although this method could not be applied directly to lead buttons, because of the insolubility of lead halides, it seemed probable that a cation exchanger could be used to remove lead selectively from the nitric acid parting solution. This approach was investigated by the following procedure.

The lead button, containing only palladium, was parted with 1:2 nitric acid, and the resulting solution was treated with a filtered solution containing 0.5 g of the disodium salt of 1,2-diaminocyclohexanetetra-acetic acid in 15–20 ml of water. The pH was adjusted to 0.5–1.0 by sodium hydroxide, and the solution was heated on a hot plate for 15–20 min to complex the palladium. After

cooling, the solution was passed through a cation-exchange column containing 50 W × 8 cation-exchange resin sufficient in quantity to adsorb approximately 30 g of lead. To remove the palladium, 3 litres of 1M nitric acid were passed through the column slowly. Lead remained adsorbed, and was stripped by passing 3 litres of 3M nitric acid through the column.

The palladium solution was evaporated almost to dryness and then transferred to a small beaker. The palladium complex was decomposed by treating with fuming nitric acid and hydrogen peroxide alternately. Finally, the palladium was dissolved by hydrochloric acid and determined gravimetrically by the sodium salt of dimethylglyoxime. The results are recorded in Table VI.

TABLE VI. SEPARATION OF PALLADIUM FROM LEAD BY ION EXCHANGE

Palladium added, <i>mg</i>	Palladium found, <i>mg</i>	Error, <i>mg</i>
9.94	9.85	0.09
9.94	9.86	0.08
4.97	4.87	0.10

Separation of the palladium from lead by precipitation

Beamish and coworkers⁹ have reported the separation of palladium from large quantities of the lead by precipitating the former with salicylaldehyde after the removal of nitric acid by evaporation of the parting solution. In the present investigation, an attempt was made to separate palladium without a prior evaporation. Preliminary experiments indicated that ascorbic acid could be employed successfully for the gravimetric determination of palladium in an acetic acid medium, and that the large quantities of nitrates did not interfere. The following procedure was applied successfully for the separation of palladium from the parting acid.

Following the dissolution of the lead button by nitric acid, sodium hydroxide was added to neutralise the solution as indicated by the appearance of a permanent precipitate, acetic acid was added to dissolve the precipitate and the resulting solution was warmed. After addition of 0.5 g of ascorbic acid, the solution was heated for a few minutes, and the precipitate was allowed to settle. The precipitate was filtered, and the residue was washed thoroughly to remove all of the lead salts. The residue was dried, ignited at 600°, dissolved by *aqua regia*, and finally treated with hydrochloric acid containing a little sodium chloride. Palladium was determined gravimetrically by the sodium salt of dimethylglyoxime. The results are listed in Table VII.

TABLE VII. SEPARATION OF PALLADIUM FROM LEAD BY PRECIPITATION

Palladium added, <i>mg</i>	Palladium found, <i>mg</i>	Error, <i>mg</i>
9.94	9.81	0.13
9.94	9.84	0.10
9.94	9.90	0.04

DISCUSSION

Irrespective of the lack of an integrated procedure for the determination of the seven noble metals in a lead button, there is value in a simple wet method for the determination of platinum, palladium, rhodium and iridium in lead buttons. By far the larger proportion of the world's supply of platinum metals is derived from deposits in which platinum and palladium predominate, with a minor proportion of the more insoluble platinum metals. The fire-assay procedure described above allows an acceptably quantitative recovery of the four metals from a lead button without the cumbersome removal of lead as the sulphate, required by the classical procedure.

One may hope for an extension of the above procedure to include consecutive determinations of osmium and ruthenium. Although these metals are collected quantitatively by lead, the only existing method for their subsequent determination involves parting with perchloric acid, followed by simultaneous isolation of both

osmium and ruthenium as tetroxides. Unfortunately, there is no established procedure recorded for a nitric acid parting of the lead button and the subsequent distillation of the octavalent oxides. It would seem reasonable that the osmium in the nitric parting solution could be oxidised to remove osmium quantitatively and selectively. However, the presence of the large amounts of lead in the parting solution may well vitiate this separation as a quantitative procedure. Furthermore, no procedure has been developed for the subsequent removal of ruthenium in a lead nitrate-nitric acid parting medium. With the accomplishment of these separations a most useful assay procedure would be available.

Acknowledgement—The authors wish to acknowledge the help rendered by Professor R. E. Jervis of the Department of Chemical Engineering of the University of Toronto in the neutron-activation analysis.

Zusammenfassung—Eine Schmelzmethode wird beschrieben, bei der Platin, Palladium, Rhodium oder Iridium in der salpetersauren Scheidelösung aus dem Bleiregulus bestimmt werden. Palladium ist das einzige Metall, das von der Scheidelösung völlig gelöst wird; Spuren von Platin und Rhodium werden mit gelöst. Die Anwesenheit von Kupfer im Bleiregulus begünstigt die Auflösung von Platin und Iridium in der Scheidelösung; Rhodium wird nicht angegriffen. Auch Ionenaustausch- und Fällungsmethoden zur Palladium-Platin-Trennung werden berücksichtigt. Es wurde versucht, die Ursache der Iridiumverluste zu ergründen, die für die klassischen Schmelzproben charakteristisch sind.

Résumé—On décrit une méthode de fusion plombeuse pour doser le platine, le palladium, le rhodium ou l'iridium dans la solution nitrique de séparation obtenue à partir du bouton de plomb. Le palladium est le seul métal complètement attaqué par la solution de séparation; on dissout aussi des traces de platine et de rhodium. On a trouvé que la présence de cuivre dans le bouton de plomb favorise la dissolution du platine et de l'iridium dans la solution nitrique de séparation; le rhodium reste inattaqué. On décrit également les techniques d'échange d'ions et de précipitation pour séparer le palladium du plomb. On a fait des essais en vue d'identifier la source de la perte en iridium, qui est une caractéristique des méthodes de dosage par fusion plombeuse.

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SHORT COMMUNICATIONS

A new class of adsorption indicators

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FAJANS¹ first suggested the use of certain luminescent dyestuffs as adsorption indicators in argentimetry. Their action is based on the disappearance of luminescence from solution at the equivalence point. This is brought about by adsorption of the dyestuff because of a change in the surface charge of the precipitate. Reversal of the charge of the precipitate causes desorption of the dyestuff and reappearance of luminescence.²

During investigations on the luminescence of cyanine dyes,³ the experiment of using some of them as adsorption indicators was carried out. For this purpose the cyanometric method⁴ was chosen; this can be used for the rapid determination of silver in light-sensitive precipitates of silver halides. As indicator a few drops of a saturated methanolic solution of a dyestuff were used. It was found that some of the dyestuffs were adsorbed on a precipitate of silver iodide and showed a strong fluorescence when excited with an ultraviolet lamp. This was observed with 1,1-dimethylbenzoxacyanine iodide (I), 1,1-dimethylbenzthiacyanine iodide (II) and many other oxacyanines and thiacyanines, prepared by the method of Fischer and Hamer.⁵

When using dyestuff (I) in the titration with 0.002*N* silver nitrate solution, the addition of 1 drop (0.05 ml) of titrant in excess causes the precipitation of silver iodide and the appearance of fluorescence. Titration can therefore be carried out in very dilute solution. If the titration is continued past the end-point, the intensity of fluorescence decreases as the silver iodide precipitate increases. This shows that the indicator is adsorbed on the initial precipitate and the light is scattered by the silver iodide subsequently precipitated. The addition of an excess of cyanide solution causes dissolution of the precipitate of silver iodide and disappearance of the fluorescence. After further addition of silver ions the fluorescence reappears instantly as silver iodide is again precipitated.

The fluorescence appears rapidly at the beginning of the precipitation, increases for a few sec, then remains constant. At low concentration of indicator the fluorescence is bluish-white, but with increasing indicator concentration there is a change towards green. Before the precipitation of silver iodide, the system (excited with an ultraviolet lamp) shows a violet fluorescence.

In the determination of silver in light-sensitive precipitates of silver halides in industrial laboratories, cases are sometimes encountered in which coloured or sparingly soluble compounds are also present. An accurate end-point cannot then be detected because the reprecipitated silver halide is obscured. In the presence of a fluorescent adsorption indicator, however, an accurate determination becomes possible.

The fluorescence from the adsorbed dyestuff (I) is quite selective. Precipitation of silver bromide in the presence of this indicator gives a green fluorescence, weaker than that with precipitates of silver iodide. In the case of silver chloride the precipitate shows only a trace of fluorescence.

Dyestuff (II) acts very slowly as a fluorescent indicator, apparently because of its low solubility in the system under investigation. Addition of a saturated methanolic solution of the dyestuff to an aqueous medium brings about partial precipitation of the solid dyestuff, showing a pink fluorescence. If silver iodide is precipitated in this system the pink fluorescence slowly changes to an intense yellow-green. This points to a change in form of the precipitated dyestuff to a more stable state of aggregation in the adsorbed form.

On filtering off silver iodide precipitated in the presence of dyestuff (I), it showed a strong fluorescence. The fluorescent emission curve obtained (Fig. 1) leads to the conclusion that there is a luminescence of the second type,⁶ which is to be attributed to the polymeric form of the dyestuff. Such polymers are often formed in systems of monomethinecyanine dyestuffs containing water⁷ and they are recognised by the Jelley adsorption band.⁸

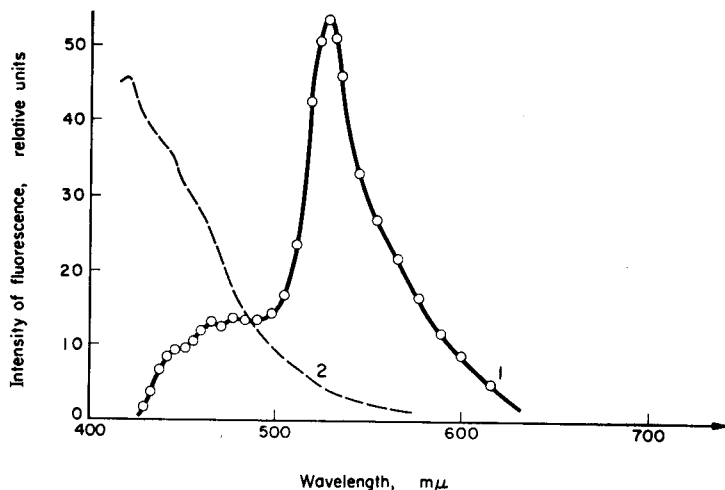


FIG. 1.—Fluorescent emission curves:
 1—silver iodide precipitated in presence of dyestuff (I) (polymeric form),
 2—filter paper stained with dyestuff (I) (monomeric form).

It is very interesting that cyanine dyestuffs fluoresce on silver iodide particles, *i.e.*, on a carrier which is known to absorb very easily the excitation energy of the dyestuff adsorbed on its surface.⁹

A more detailed account of the above investigations will be published in due course.

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Summary—Oxacyanine and thiacyanine dyes have been found to act as fluorescent adsorption indicators in the cyanometric titration of silver halides.

Zusammenfassung—Oxacyanin- und Thiacyaninfarbstoffe wirken als fluoreszierende Adsorptionsindikatoren bei der cyanometrischen Titration von Silberhalogeniden.

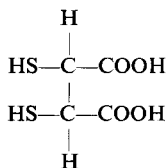
Résumé—On a trouvé que les colorants de l'oxacyanine et de la thiacyanine se comportent comme indicateurs d'adsorption fluorescents dans le dosage cyanométrique des halogénures d'argent.

Use of masking agents in chelatometric titrations—IV:* Dimercaptosuccinic acid†

(Received 6 May 1964. Accepted 7 July 1964)

IN continuation of our investigations on the use of mercaptans as masking agents in chelatometric titrations, the properties of dimercaptosuccinic acid (DMS) have now been investigated. Although the antimony complex of DMS has been used as a chemotherapeutic agent for certain tropical diseases, the only paper which has discussed the chelating behaviour of DMS is that of Agren and Schwarzenbach, who investigated the chelation with zinc.¹

DMS is a tetradentate ligand having two carboxylic acid and two mercapto groups:



However, all of these functional groups cannot co-ordinate with the same metal ion. As might be expected, most DMS-metal chelates are soluble in water. Although the co-ordinating groups of DMS are the same as those of thioglycolic acid or β -mercaptopropionic acid, differences in the number of co-ordinating groups and their steric arrangement will lead to a different selectivity of masking in EDTA titrations.

EXPERIMENTAL

Reagents

Dimercaptosuccinic acid (DMS):‡ This was synthesised from acetylenedicarboxylic acid and thioacetic acid according to the procedure of Gerecke, Friedheim and Brossi.² As is clear from the structure of DMS, four modifications (d, l, racemic and meso) are possible. However, only two of these (racemic and meso) have so far been known. The reported melting points for the pure isomers are 210–1° (meso form) and 127–8° (racemic form). The material used in this experiment has a melting point of 195–7° and is believed to consist mostly of meso form.

DMS is a white crystalline solid which is rather unstable and easily oxidised in the air. It has no objectionable odour. In the present experiments, a 0.1M methanolic solution of the disodium salt of DMS was employed. The methanolic solution can be stored for more than a month, if it is kept in a refrigerator in a sealed bottle. If it is used frequently in the laboratory, however, the solution should be prepared each week.

Buffer solutions: A standard composition of aqueous ammonia and ammonium chloride was used for pH 10 and hexamethylenetetramine for pH 6.

Indicator solutions: Eriochrome Black T (0.5% in methanol with an addition of hydroxylamine hydrochloride) and Xylenol Orange (0.1% aqueous) were used.

Solutions of cations and EDTA were prepared in 0.01M concentration from reagent-grade chemicals, and their strengths determined against primary standard metallic zinc.

Preliminary investigation

In order to estimate the selectivity of masking by DMS, the following experiments were carried out:

One ml of a 0.01M cation solution was diluted to 50 ml, and to this were added 1 ml of DMS solution and 1 ml of buffer solution. Tests were also carried out in the presence of Xylenol Orange or Eriochrome Black T indicator both with and without the addition of DMS. The resulting colours of the solutions were compared.

As pointed out in a previous paper,³ this test does not always suggest the possibility of masking in the EDTA titration of certain metals. However, it can be a useful guide in the screening test of masking agents. The results are shown in Table I.

* Part III: *Talanta*, 1963, 10, 1195.

† Contribution No. 50 from Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Japan.

‡ Now available from Dôjindô and Co., Kumamoto, Japan, in reagent-grade form.

TABLE I

Metal ion	With Xylenol Orange at pH 6				With Eriochrome Black T at pH 10			
	(1)	(2)	(3)	Masking against XO	(1)	(2)	(3)	Masking against Erio T
Al	colourless	red	red	no	colourless	violet	violet	no
Ca	colourless	—	—	—	colourless	red-violet	red	no
Cd	colourless	yellow	red	yes	colourless	blue	violet	yes
Co	brown	ND	red-violet	?	yellow-brown	green	violet	yes
Cu ²⁺	yellow	yellow	red	yes	yellow	blue-green	violet	yes
Fe ³⁺	red-brown	ND	red	?	red	ND	violet	?
Hg ²⁺	colourless	yellow	red	yes	colourless	blue-violet	violet	no
Mg	colourless	—	—	—	colourless	red	red	no
Mn ²⁺	colourless	violet	violet	no	brown	green	violet	yes
Ni	green	ND	violet	?	dark green	green	violet	yes
Pb	colourless	yellow	violet	yes (not quantitative)	colourless	blue	red	yes
Zn	colourless	red	red	no	colourless	blue	red	(not quantitative)

(1) Colour reaction observed after adding buffer and DMS to the metal ion solution.

(2) Colour reaction observed after adding indicator to the solution in (1).

(3) Colour reaction observed after adding buffer and indicator to the metal ion solution.

ND: Coloration of metal-DMS complex so intense that no distinct colour of indicator can be observed.

Titration of zinc in presence of cadmium or copper(II)

To a mixture of 10 ml of a 0.01M solution of zinc and 1–5 ml of a 0.01M solution of cadmium or 2–6 ml of a 0.01M solution of copper(II), 2–4 ml of DMS solution, about 100 mg of hexamethylenetetramine and a few drops of Xylenol Orange indicator solution were added. After diluting to 100 ml, the solution was titrated with 0.01M EDTA solution.

Titration of magnesium in presence of various bivalent cations

A similar procedure to that for the titration of zinc was followed, except that the pH was adjusted to 10 with 3 ml of ammoniacal buffer solution and Eriochrome Black T indicator was used as indicator.

The results of the titrations are summarised in Tables II and III.

TABLE II.—TITRATION OF ZINC AT pH 6

Zn taken, mg	Metal present, mg	0.1M DMS added, ml	Zn found, mg	Error, mg
	Cd			
6.67	1.12	2	6.73	+0.06
6.67	2.24	4	6.75	+0.08
6.67	3.36	4	6.85	+0.18
6.67	5.60	4	6.78	+0.11
	Cu			
6.67	1.27	2	6.58	–0.09
6.67	3.18	3	6.51	–0.16
	Hg			
6.70	10.0	a	6.68	–0.02
6.70	20.0	a	6.67	–0.03

^a A large excess of DMS tends to give a negative error. DMS solution should be added dropwise until the disappearance of the white precipitation which first forms.

TABLE III.—TITRATION OF MAGNESIUM AT pH 10

Mg taken, mg	Metal present, mg	0.1M DMS added, ml	Mg found, mg	Error, mg
	Pb			
2.44	10.36	7	2.44	0
2.44	20.72	12	2.46	+0.02
	Cu			
2.44	0.64	1	2.40	-0.04
2.44	1.27	2	2.40	-0.04
2.44	3.18	4	2.39	-0.05
2.44	6.35	5	2.37	-0.07
	Ni			
2.44	0.59	2	2.41	-0.03
	Co			
2.44	0.59	1	2.41	-0.03
2.44	1.18	2	2.41	-0.03
2.44	1.77	3	2.40	-0.04
	Cd			
2.44	11.24	15	2.42	-0.02

RESULTS AND DISCUSSION

Use of DMS at pH 6

Zinc can be titrated selectively in the presence of cadmium, if the amount of the latter does not exceed that of the zinc. Increasing positive errors are noted with an increasing amount of cadmium. These errors may be caused by indistinct colour change near the end-point, because the pure yellow colour is only observed slightly after the equivalence point. As to the selective titration of zinc in the presence of cadmium, Přibil has proposed a method in which a selective replacement reaction of cadmium-EDTA complex with diethyldithiocarbamate is utilised.⁴ The present method is simpler and can be readily adapted to practical applications.

Copper can also be masked up to one half of the amount of zinc. In this case, however, the titration errors tend to be negative, and the reason may be that the yellow coloration of the copper-DMS complex tends to give an earlier end-point with Xylenol Orange. From Table I it seems that lead can also be masked with DMS. However, the complex is insufficiently stable to be masked against EDTA titration.

Iron(III), cobalt and nickel form coloured complexes with DMS in this pH region, and their colours are so intense that no distinct end-point colour change can be observed.

Use of DMS at pH 10

Lead, copper(II), nickel, cobalt and cadmium can be masked in the presence of the alkaline earth metals. Because lead and cadmium form colourless complexes with DMS, even large amounts of them can be masked efficiently. Copper(II) forms a yellow complex at pH 10, and negative errors are noted because of the earlier end-point. Although from Table I zinc can be masked against the indicator, the zinc-DMS complex is insufficiently stable to be masked against EDTA. Nickel and cobalt form dark green and brown complexes, respectively, and they must not be present in large amount. Iron(III) forms a dark red complex even in the presence of triethanolamine and must, therefore, be absent when DMS is employed as a masking agent.

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Summary—Dimercaptosuccinic acid has been examined as a masking agent in EDTA titrations. At pH 6 it is possible to determine zinc in the presence of cadmium, copper(II) and mercury(II). At pH 10 most bivalent cations except for the alkaline earth metals can be masked.

Zusammenfassung—Der Gebrauch von Dimercaptobernsteinsäure als Maskierungsmittel bei EDTA-Titrationen wurde studiert. Mit diesem Reagens kann Zink bei pH 6 neben Cadmium, Kupfer(II) und Quecksilber(II) bestimmt werden. Bei pH 10 können außer Erdalkalien die meisten zweiwertigen Kationen mit diesem Reagens maskiert werden.

Résumé—On a étudié l'acide dimercaptosuccinique en tant qu'agent de dissimulation dans les dosages à l'EDTA. En utilisant ce réactif à pH 6, on peut doser le zinc en présence de cadmium, cuivre(II) et mercure(II). A pH 10, la majeure partie des cations divalents, à l'exception des ions alcalino-terreux, peut être dissimulée par ce réactif.

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A specific method for the determination of trace amounts of titanium

(Received 18 May 1964. Accepted 29 July 1964)

WHILE attempting to devise a method for the simultaneous determination of titanium and zirconium,¹ a specific method for determining trace amounts of the former element has been developed. Titanium is precipitated from a hydrochloric-sulphuric acid medium with cupferron using zirconium as a collector. A hydrochloric-hydrofluoric acid solution, containing the titanium and other elements precipitated quantitatively or partly with cupferron, is passed through a column containing Dowex-1 \times 8 anion-exchange resin.^{2,3} Niobium and tantalum are retained by the resin. Titanium and the remaining elements pass unadsorbed into the eluate, from which titanium is again precipitated with cupferron. Titanium is separated from tungsten and molybdenum by precipitation with sodium hydroxide using iron as a collector. The determination is completed colorimetrically after extraction of the titanium-thiocyanate complex with a solution of tri-*n*-octylphosphine oxide in cyclohexane.⁴ The method is accurate to within $\pm 5\%$ (relative) or $\pm 0.75 \mu\text{g}$ of titanium, whichever is greater.

EXPERIMENTAL

Reagents

Hydrofluoric acid, 29M

Hydrochloric acid, 1.2M and 12M

Sulphuric acid, 3.6M, 6M and 18M

25% *Hydrochloric acid*-20% *hydrofluoric acid*

Filter paper, Whatman No. 40, 5.5 cm and 12.5 cm. Filter paper has been found to be the major cause of high blanks. If Whatman papers are unavailable, the papers to be used should be analysed for titanium before application of the procedure.

Filter paper pulp. Cut Whatman 40 filter paper into small (1 cm \times 1 cm) pieces and shake vigorously with hot water in a stoppered Erlenmeyer flask.

Zirconium sulphate solution, 1 mg of zirconium/ml

Iron(III) chloride solution, 10 mg of iron/ml

Cupferron solution, 6% (w/v), freshly prepared

Cupferron wash solution. Add 10 ml of 6% cupferron solution to 500 ml of 1.2M hydrochloric acid. Prepare just before use.

Sodium bisulphate

Anion-exchange resin. Dowex 1 \times 8, 100-200 mesh resin obtained from Bio-Rad Laboratories.

Sodium hydroxide, 1% and 40% solutions

Citric acid

Thioglycolic (mercaptoacetic) acid, 98% solution

Ammonium thiocyanate

Tri-n-octylphosphine oxide (TOPO), 0.01M in cyclohexane

Standard titanium solution. Prepare a standard titanium solution containing 5 μ g of titanium/ml in 6M sulphuric acid.

Procedure

Dissolve the sample, preferably containing a minimum of 15 μ g of titanium, and obtain it in 150 ml of solution containing 10 ml of hydrochloric acid and 25 ml of sulphuric acid. Add 10 ml of zirconium sulphate solution and 0.5 g of filter paper pulp. Cool the sample solution, the 6% cupferron solution and the cupferron wash solution to 10–15°. Add 15 ml of cupferron solution, or sufficient to obtain complete precipitation, and filter. (It is very convenient to filter through a 6.3-cm i.d. Büchner funnel using suction. A piece of 5.5-cm filter paper is first placed in the bottom of the funnel, then a piece of 12.5-cm paper is pushed down into the funnel using a 150-ml beaker. Finally, with the suction on, the paper is wetted with water.) Wash the precipitate 10 times with the cupferron wash solution. Transfer the precipitate to a platinum crucible and ignite. Fuse the residue in about 2 g of sodium bisulphate. Dissolve the melt in a polyethylene beaker with 50 ml of 25% hydrochloric-20% hydrofluoric acid, warming gently. Pass 50 ml of the hydrochloric-hydrofluoric acid solution through the anion-exchange column (12 cm \times 1 cm i.d., containing 8 cm of anion-exchange resin) and discard the eluate. Pass the sample solution through the column and wash with 50 ml of the same eluent, collecting the eluate in a platinum dish. Add 5 ml of sulphuric acid and heat to fumes of sulphuric acid. Transfer the solution to a 250-ml beaker and dilute to about 100 ml with water. Cool, add 5 ml of 12M hydrochloric acid, 0.5 g of filter paper pulp and 15 ml of 6% cupferron solution. Filter as described and wash the precipitate 5 times with the cupferron wash solution.

Ignite the precipitate in a platinum dish or crucible, cool and dissolve the residue with 10 ml of hydrofluoric acid. Add 2 ml of sulphuric acid and evaporate to fumes of sulphuric acid. Cool, add 15 ml of water and warm to dissolve the salts. Add 1 ml of the iron(III) chloride solution and transfer the solution to a 50 ml centrifuge tube containing 20 ml of 40% sodium hydroxide. Mix, cool and centrifuge. Decant the supernatant solution, add 30 ml of 1% sodium hydroxide, mix, centrifuge and again discard the solution. Add 15 ml of 6M sulphuric acid to dissolve the basic salts and transfer with 6M sulphuric acid to a 125-ml separatory funnel. (If the sample is known to contain more than 15 μ g of titanium, transfer the solution to a volumetric flask, dilute with 6M sulphuric acid, and use an aliquot containing 15 μ g of titanium.)

Add sufficient 6M sulphuric acid to the separatory funnel to obtain a volume of about 35 ml. Add 1 g of citric acid, 1 ml of thioglycolic acid and 3 g of ammonium thiocyanate. Stopper the funnel and shake for 30 sec to dissolve the salts. Add exactly 15 ml of 0.01M TOPO solution, stopper the funnel and shake for 5 min.* Allow the layers to separate, and draw off and discard the aqueous layer. Wash the organic phase for 1 min with 35 ml of 6M sulphuric acid. Discard the acid wash. Draw the organic phase into a 15-ml glass-stoppered centrifuge tube and centrifuge the extract for 1 min. Measure the absorbance of the extract in a 1-cm cell at 429 m μ using cyclohexane in the reference cell. (At this wavelength, the molar absorptivity of the complex is about 43,000, indicating an absorbance of about 0.9 for 1 μ g of titanium/ml in 1-cm cells. The extracted complex is stable, within experimental error, for at least 24 hr. The absorbance is a linear function of concentration, at least from 0 to 1 μ g of titanium/ml, and obeys Lambert's law when 1-, 2-, and 5-cm cells are used.) Determine the titanium concentration by reference to a standard curve obtained by carrying known amounts of titanium in 6M sulphuric acid through the extraction steps. (It is, of course, desirable that one determine both a reagent blank and a recovery figure for the entire procedure.)

No interference was caused by the presence of 10-mg amounts of Al, Sb^{III}, As^{III}, Ba, Be, Bi, B, Br (as Br⁻), Cd, Ca, Ce^{IV}, Cs, Cr^{III} Co, Cu^{II}, Dy, Er, Eu, F (as F⁻), Gd, Ga, Ge, Au, Hf, Ho, In, I (as I⁻), Ir, Fe^{III}, La, Pb, Li, Lu, Mg, Mn^{II}, Hg^{II}, Mo, Nd, Ni, Nb, N (as NO₃⁻), Pd^{IV}, P (as PO₄³⁻), Pt^{IV}, K, Pr, Re, Rh, Rb, Sm, Sc, Se^{IV}, Si, Ag, Na, Sr, Ta, Te^{IV}, Tb, Tl^I, Th, Tm, Sn^{IV}, W, U^{VI}, V^V, Yb, Y, Zn or Zr.

* The extraction of titanium is discussed in considerably more detail in reference 1.

Procedure modifications

(1) If niobium and tantalum are known to be absent in interfering amounts,¹ the ion-exchange step may be omitted. After the initial precipitation of titanium, ignite the precipitate and fuse the residue in a minimum amount of sodium or potassium bisulphate. Dissolve the fused mass with 15 ml of 3.6*M* sulphuric acid, add 1 ml of iron(III) chloride solution and transfer to a 50-ml centrifuge tube containing 20 ml of 40% sodium hydroxide. Continue with the procedure as described.

(2) If tungsten and molybdenum are known to be interfering amounts,¹ the sodium hydroxide precipitation step may be omitted. Dissolve the first cupferron precipitate, after ignition, with the hydrochloric-hydrofluoric acid solution and perform the ion-exchange separation as described. Add 2 ml of sulphuric acid to the eluate and evaporate to fumes of sulphuric acid. Continue with the extraction of titanium as described.

(3) If niobium, tantalum, molybdenum and tungsten are all absent, both the ion-exchange and sodium hydroxide precipitation steps can be omitted. The precipitate can be ignited, treated with hydrofluoric and sulphuric acids, evaporated to fumes of sulphuric acid, and extracted. If barium, tin and antimony are also absent, the precipitate can be destroyed by treatment with nitric and perchloric acids as described in reference 1.

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Summary—A method is presented which is specific for the determination of trace amounts of titanium. Titanium is precipitated with cupferron using zirconium as a collector. Further separation from interfering elements is made by anion exchange and precipitation with sodium hydroxide using iron as a collector. The determination is completed colorimetrically after extraction of the titanium-thiocyanate complex with a solution of tri-*n*-octylphosphine oxide in cyclohexane. The method is accurate to within $\pm 5\%$ (relative) or $\pm 0.75 \mu\text{g}$ of titanium, whichever is greater.

Zusammenfassung—Eine spezifische Methode zur Bestimmung von Titanspuren wird angegeben. Titan wird auf Zirkontrager mit Cupferron gefällt. Durch Anionenaustausch und Fällung mit Natriumhydroxyd auf Eisentrager werden weitere störende Elemente abgetrennt. Bestimmt wird Titan durch Extraktion seines Rhodanidkomplexes mit Tri-*n*-octylphosphinoxid in Cyclohexan. Die Methode ist auf $\pm 5\%$ (relativ) oder bestenfalls $\pm 0,75 \mu\text{g}$ genau.

Résumé—On présente une méthode de dosage spécifique du titane à l'état de traces. On précipite le titane au cupferron en utilisant le zirconium comme agent collecteur. On procède ensuite à une séparation des éléments interférants par échange anionique, et précipitation à la soude, en utilisant le fer comme agent collecteur. On effectue le dosage par extraction du complexe thiocyanique du titane au moyen d'une solution d'oxyde de tri-*n*-octylphosphine en cyclohexane. La précision de la méthode est $\pm 5\%$ en valeur relative ou $\pm 0,75 \mu\text{g}$ de titane. On prend la plus grande des deux erreurs.

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Response rates of cation-sensitive glass electrodes

(Received 30 May 1964. Accepted 7 July 1964)

THE response-rate characteristics of cation-sensitive glass electrodes ultimately determine the applicability of such electrodes to dynamic concentration measurements in continuous analysis or kinetic studies. Several authors^{1,2} have noted the apparently sluggish response of cation-sensitive glass electrodes to rapid concentration changes in aqueous solution; in a previous paper,³ we also reported response times of the order of several minutes for the Beckman 78137 V experimental electrode. In the light of modern evidence⁴ on the nature of the potential-determining mechanism of both pH-type and cation-sensitive glass electrodes, it seems likely that the slow response of the latter results from poor construction characteristics and pretreatment, rather than from any inherent slow steps in the response mechanism. Because considerable technical advances in the manufacture of cation-sensitive glass electrodes have been achieved since our previous report, the response characteristics of the newest commercially available electrode were re-examined to test this hypothesis.

EXPERIMENTAL

Measurements were carried out in stirred solution, using the new Beckman 39137 cationic glass electrode. Potentials (*versus* Beckman 39170 fibre-junction calomel reference electrode) were determined with a Beckman Model 76 expanded-scale pH meter; the electrode response was timed with a stopwatch. The inherent deflection time of the pH meter was found to be 0.8 ± 0.1 sec per 100 mv on the expanded scale.

Electrode-response measurements were carried out by two procedures, employing (1) a dipping and (2) a dilution method. In all cases, the glass electrode was preconditioned by a 24-hr soaking in the appropriate reference solution. Experiments were performed at room temperature because changes in ambient temperature were negligible during the times involved.

Dipping procedure: Immerse the glass-calomel electrode pair in the stirred reference solution and measure the equilibrium potential. Transfer the glass electrode to the test solution containing the metal ion in a concentration greater than, smaller than, or equal to that of the reference solution.

TABLE I.—RESPONSE OF CATION-SENSITIVE GLASS ELECTRODE TO CONCENTRATION CHANGES

(1) Dipping experiments					
Metal ion	Solution concentrations, moles/litre			Response times, sec	
K ⁺ (KCl)	Reference	Test	Reference		
		0.5 \xrightarrow{t}	0.5	1.6	
		0.1 \xrightarrow{t}	0.1	1.5	
		0.5 \xrightarrow{t}	1.0 \xrightarrow{t}	0.5	1.6
		0.5 \xrightarrow{t}	0.0 \xrightarrow{t}	0.5	2.5
		0.1 \xrightarrow{t}	1.0 \xrightarrow{t}	0.1	3.1
		0.1 \xrightarrow{t}	0.05 \xrightarrow{t}	0.1	2.3
		0.1 \xrightarrow{t}	0.0 \xrightarrow{t}	0.1	2.6
	Na ⁺ (NaCl)		1.0 \xrightarrow{t}	1.0	1.6
			0.1 \xrightarrow{t}	0.1	1.6
		1.0 \xrightarrow{t}	0.1 \xrightarrow{t}	1.0	2.4
		1.0 \xrightarrow{t}	0.0 \xrightarrow{t}	1.0	2.5
		0.1 \xrightarrow{t}	1.0 \xrightarrow{t}	0.1	3.1
		0.1 \xrightarrow{t}	0.0 \xrightarrow{t}	0.1	2.3
(2) Dilution experiments					
Metal ion		Solution concentrations, moles/litre			Response times, sec
K ⁺ (KCl)		1.0 \xrightarrow{t}	0.5	2.9	
		1.0 \xrightarrow{t}	0.5	3.9	
		0.1 \xrightarrow{t}	0.05	3.1	

After 30 sec return the glass electrode to the reference solution and measure the time, t , required for the indicated potential to return to within ± 0.5 mv of the equilibrium value.

Dilution procedure: With the glass-calomel electrode pair in the stirred reference solution and at equilibrium, rapidly add an equal volume of distilled water to the cell and measure the time, t , required for the indicated potential to come within ± 0.5 mv of the expected value (determined by prior equilibrium measurements in solutions of appropriate concentration).

RESULTS AND DISCUSSION

The results of the dipping and dilution experiments are given in the Table I. The reported response times are, in each case, the mean of at least 4 measurements, and have an experimental uncertainty of about 0.2 sec. In the dilution experiments, an added uncertainty may result from the difficulty of effectively mixing two solutions of appreciable volume (50 ml) within a fraction of a second.

The response rates determined are considerably faster than those observed with the earlier types of cation-sensitive electrodes, and approach the response limitations of the usual potentiometric measurement systems. As expected, electrode recovery times increase as the ionic environment is changed more and more drastically, but response times are compatible with the requirements of continuous analyses or kinetic studies where concentrations may change rapidly over moderate ranges. The results suggest that first-order reactions with rate constants as large as 0.4 sec^{-1} could be effectively monitored using the cation-sensitive glass electrode.

Acknowledgement—The financial support of NIH Grant GM-10086 is gratefully acknowledged.

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Summary—A re-evaluation of the response of cation-sensitive glass electrodes to rapid concentration changes indicates typical response times in the 1.5–4.0 sec range and suggests that such electrodes might be used for continuous analyses or for reaction rate studies.

Zusammenfassung—Eine Neubestimmung des Ansprechens kationempfindlicher Glaselektroden auf schnelle Konzentrationsänderungen zeigt typische Ansprechzeiten in der Gegend um 1,5–4,0 Sekunden. Demnach bieten sich solche Elektroden zu kontinuierlichen Analysen oder zur Untersuchung von Reaktionsgeschwindigkeiten an.

Résumé—Une nouvelle évaluation de la réponse des électrodes de verre catio-sensibles aux variations rapides de concentration montre des temps de réponse caractéristiques entre 1,5 et 4 secondes, et suggère que de telles électrodes peuvent être employées pour des analyses en continu ou des études de vitesse de réaction.

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LETTER TO THE EDITOR

The international nature of *Talanta*

SIR,

The ever increasing amount of scientific research has resulted in a constant rise in the number of journals available for its publication. One of the newer journals is *Talanta*, and on its cover is printed "An International Journal of Analytical Chemistry". It would be interesting to know if this declaration is really justified. Is it possible for you to provide data concerning the numbers of papers from different countries which have been published in *Talanta*?

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5 June 1964*

Dear Dr. PŘIBIL,

I hope that you will find the information for which you have asked in the Table overleaf.

CECIL L. WILSON (Editor-in-Chief)

CONTRIBUTIONS* TO THE FIRST 10 VOLUMES† OF TALANTA

Country	Volume										Contributions per country
	1	2	3	4	5	6	7	8	9	10	
	Contributions										
Australia	—	—	—	—	—	—	—	—	—	1	1
Austria	—	1	1	—	—	—	1	2	4	6	15
Belgium	1	3	1	—	—	—	—	3	3	2	13
Brazil	3	1	—	1	—	—	—	—	2	—	7
Bulgaria	—	—	—	—	—	—	—	—	2	1	3
Canada	1	2	3	3	2	3	1	1	2	6	24
Czechoslovakia	3	2	5	3	6	—	—	19	12	24	74
Finland	—	—	—	—	—	—	—	1	—	1	2
France	—	—	—	—	2	—	—	4	1	1	8
German Democratic Republic	—	1	—	—	—	—	—	—	1	1	3
German Federal Republic	—	1	1	—	—	—	—	1	—	—	3
Hungary	8	4	8	4	3	—	3	6	3	33	72
India	3	1	—	3	2	—	2	9	7	12	39
Ireland	—	—	—	—	—	—	—	—	1	—	1
Israel	1	—	—	—	2	—	1	2	1	4	11
Italy	—	—	—	—	1	—	—	1	1	—	3
Japan	3	2	5	4	5	—	—	3	9	8	39
Netherlands	—	—	—	—	—	—	—	1	1	2	4
Pakistan	—	—	—	—	—	—	—	—	—	1	1
Poland	—	3	—	1	2	—	1	1	2	4	14
Portugal	—	—	—	—	—	—	—	2	—	—	2
Rumania	—	—	—	—	1	—	3	1	—	1	6
South Africa	—	—	—	—	—	—	—	—	1	—	1
Spain	1	—	—	—	—	—	—	1	—	1	3
Sweden	—	—	2	4	—	—	—	1	—	1	8
Turkey	—	—	—	—	—	—	—	—	1	1	2
United Kingdom	15	16	15	9	7	—	3	28	51	30	174
U.S.A.	15	34	20	15	17	39	27	40	43	59	309
U.S.S.R.	—	—	—	—	—	—	—	6	6	1	13
Yugoslavia	—	—	—	—	—	—	—	1	—	—	1
Contributions per volume	54	71	61	47	50	42	42	134	154	201	856
Countries per volume	11	13	10	10	12	2	9	22	21	23	
Pages per volume	416	404	378	298	294	276	322	916	1076	1306	

* These include preliminary communications, short communications and letters.

† Monthly publication began with Volume 8.

NOTICES

(Material for this section should be sent directly to the Associate Editor)

UNITED KINGDOM

Wednesday 4 November 1964: Afternoon and evening meeting on **Toxic Substances in Air:** Society for Analytical Chemistry. Wellcome Building, Euston Road, London N.W.1, 3.00 p.m.

Friday-Saturday 12-13 November 1964: Conference on **Accuracy in X-Ray Analysis:** *Institute of Physics and Physical Society, X-Ray Analysis Group.* Institution of Mechanical Engineers, London S.W.1 (see *Talanta*, 1964, **11**, August, ii).

Thursday 19 November 1964: **Photometric Titrations:** J. B. HEADRIDGE: *Society for Analytical Chemistry, Midlands Section.* Lanchester College of Technology, Priory Street, Coventry, 7.00 p.m.

Friday 20 November 1964: **High Resolution Mass Spectrometry:** W. SNEDDON: *Society for Analytical Chemistry, North of England Section and Special Techniques Group.* The Blossoms Hotel, Chester, 6.00 p.m.

Tuesday 24 November 1964: **Annual General Meeting** followed by Film Show: *Society for Analytical Chemistry, Special Techniques Group.* Burlington House, London W.1, 7.00 p.m.

Friday 27 November 1964: **Some Aspects of Chemical Toxicological Analysis:** H. V. STREET: *Society for Analytical Chemistry, Scottish Section.* University of Strathclyde, Glasgow, 7.15 p.m.

Friday 27 November 1964: **Recent Advances in Analytical Chemistry:** T. S. WEST: *Society for Analytical Chemistry, Western Section and Royal Institute of Chemistry, Cardiff and District Section.* College of Technology, Newport, 6.30 p.m.

British Standards Institution has announced the following New British Standards:

B.S. 3599/6-15: 1964: *Organic pigments for paints.* C.I. Pigment Red 12 (Bordeaux F2R), C.I. Pigment Red 112 (Red FGR), C.I. Pigment Red 10 (Red FRL), C.I. Pigment Red 7 (Red F4RH), C.I. Pigment Red 9 (Red FRL), C.I. Pigment 5 (Carmine FB), C.I. Pigment Green 7 (Polychloro-copper phthalocyanine), C.I. Pigment Blue 15 (Copper phthalocyanine), C.I. Pigment Green 10 (Nickel azo yellow), C.I. Pigment Yellow 12 (Benzidine yellow).

Residue on sieve, sulphated ash, matter volatile at 100°, matter soluble in water and pH of aqueous extract, oil absorption value, colour, staining power and colour on reduction, fastness to light, bleeding, heat stability and resistance to acids and alkalis, determination of copper content. Stability of C.I. Pigment Blue 15. (Price: 17s. 6d.)

B.S. 3762: 1964: *Methods of sampling and testing detergents.*

Part 1, two sampling methods for powders from packets;

Part 2, analytical methods in four sections; A: two qualitative test methods; B: seventeen methods for schematic examination of active matter; C: nine other methods for analysis of active matter; D: fourteen methods for determination of constituents other than active matter.

Part 3, nine test methods for physical properties and performance.

Appendices: special reagents, three methods of preparation and one specification. (Price £2. 2s.)

The following *Revised British Standards* have been announced:

B.S. 903: Methods of testing vulcanized rubber: Part B14: 1964: *Determination of carbon black (replacing Part 7 of B.S. 903: 1950).* This covers three methods of determining carbon black with details of reagents, apparatus and procedure. (Price: 10s.)

B.S. 2690: Methods of testing water used in industry: Part 1: 1964: *Copper and iron.* This details three methods for copper and two methods for iron. (Price: 6s.)

The following *Amendment Slips* have been announced:

- B.S. 1728: *Methods for the analysis of aluminium and aluminium alloys: Part 5: 1953: Copper (absorptiometric method). Amendment No. 1: PD 5267.*
 B.S. 2782: *Methods of testing plastics. Part 4: Analytical methods and viscosity in solution. Amendment No. 10: Methods 405 and 406: PD 5283. (Price: 10s.)*

UNITED STATES OF AMERICA

Wednesday–Friday 21–23 October 1964: Twelfth Detroit Anachem Conference. McGregor Memorial Conference Centre, Wayne State University, Detroit, Michigan.

The programme is as follows:

Wednesday Morning, October 21: Significance of Spectroscopic Methods to Clinical and Biological Research

Interpretation of analytical data in clinical and biological research.

H. MITCHELL PERRY, JR.

Standardisation problems in analysis of biological samples for trace elements.

C. L. GRANT

Spectrographic determination of beryllium in air, biological materials and ores using the sustaining a.c. arc.

R. G. KEENAN and J. L. HOLTZ

The place of atomic absorption in tissue analysis.

C. FELDMAN

Lasers in emission for clinical research.

F. BRECH

Light-induced absorption changes in photosynthetic bacterial preparations.

H. E. BALES

Symposium on Thermal Methods of Analysis

New developments in "solution enthalpimetry".

J. JORDAN and P. T-S PEI

A critical evaluation of experimental variables in DTA.

J. R. SCHEMPF, F. M. ANGELONI
and F. E. FREEBERG

Evaluation of solid state phase transformations by DTA and dilatometry.

S. GORDON

Improved resolution of differential thermal analyses through use of pressure effects.

P. D. GARN

A thermoanalytical study of pyrotechnic coloured smoke compositions.

C. CAMPBELL, G. WEINGARTEN
and D. ANDERSON

Thermoparticulate analysis.

F. W. VAN LUIK, JR. and

C. B. MURPHY

Thermal analysis in phase purifications of polymorphic solids.

A. R. GLASGOW, JR.

Product control by differential scanning calorimetry.

J. L. JUSTIN and N. BRENNER

Wednesday Afternoon, October 21: Significance of Spectroscopic Methods in Clinical and Biological Research

The analytical problems in biology and medicine.

W. B. MASON

Chemical enrichment methods in spectrographic analysis.

E. E. PICKETT

X-Ray methods of elemental analysis.

T. HALL

Breath analysis: Key to diagnosis of vapour exposure.

R. D. STEWART

Symposium on Microanalysis

Microchemistry: Implications and current trends.

T. S. MA

A rapid Pregl combustion carbon-hydrogen determination.

C. E. CHILDS and E. E. MEYER

Chemical analysis of thin films.

K. L. CHENG

Role of the electron probe microanalyser in microanalytical chemistry.

A. C. OTTOLINI and

T. P. SCHREIBER

Analytical Chemistry—General

Determination of trace amounts of vanadium in steels and cast irons by amperometric titration.

F. P. VALENTE and G. H. CAREY

Cumulative coulographic titrimetry—I: Principles—II: Some new light on mercury catalysis in halogenation of unsaturated compounds: Titrations with electrogenerated bromine monochloride.

S. T. HIROZAWA

Reactions in concentrated lithium chloride solutions: Determination of free acid and hydrolysable metal.
Radio-release methods for evaluation of atmospheric pollution.

H. KUBOTA
 H. H. ROSS

Thursday Morning, October 22: Symposium on Polarography

Recent developments in stripping analysis.

I. SHAIN

Application of derivative techniques to anodic stripping voltammetry.

S. P. PERONE and J. R. BIRK

Stripping and voltammetric determination of manganese via manganese dioxide.

C. HUBER

Second derivative d.c.-polarography as a technique in quantitative polarographic measurements.

W. L. BELEW, J. D. FISHER and
 M. T. KELLEY

Pulse polarography.

E. P. PARRY, R. A. OSTERYOUNG
 and H. SCHLEIN

Recent developments in lanthanide ion polarography.

A. TIMNICK, R. F. LARGE and
 R. O'DONNELL

Polarographic reduction of pyridinium ion in pyridine: Application to determination of Bronsted and Lewis acids.

M. S. SPRITZER, J. M. COSTE and
 P. J. ELVING

Electro-oxidation of tetraphenylborate ion at the pyrolytic graphite electrode.

W. R. TURNER and P. J. ELVING

Polarographic behaviour of molybdenum(VI) in acidic chloride media.

G. A. RECHNITZ and J. WITJICK

Symposium on Organic Functional Group Analysis

New dimensions in organic functional group analysis.

S. SIGGIA

Recent advances in redox methods.

K. G. STONE

Reagents for hydroxyl group analysis.

G. H. SCHENK

Potentiometric determination of acid groups in acrylic polymers and fibers.

J. R. KIRBY and A. J. BALDWIN

Colorimetric determination of tertiary aromatic amines in primary and secondary amines using tetracyanoethylene.

P. O. WARNER and G. H. SCHENK

Determination of 18 to 22 mole ethoxymers in 9 mole ethylene oxide adduct of p-nonylphenol.

N. E. SKELLY and W. B. COMMETT

Thursday Afternoon, October 22: Anachem Award Symposium

Anachem Address: The challenge of analytical chemistry.

L. T. HALLET

Trends and problems in the literature of analytical chemistry.

W. D. COOKE

The information explosion myth.

H. S. NUTTING

Thursday Evening, October 22: Conference Address

Alpha particle analysis of surfaces: Plans for lunar missions.

A. TURKEVICH

Friday Morning, October 23: Clinical and Biochemistry Symposium

A study of determination of phosphorus in blood serum and urine.

R. E. MOSHER

Colorimetric estimation of urinary iron by a non-ashing technique.

J. F. GOODWIN

Spectrophotometric determination of p-hydroxyphenylpyruvic acid in human urine.

I. J. HOLCOMB and A. J. BOYLE

Photosynthetic nucleotide coenzyme analyses.

W. L. OGREN

A study of the Liberman colorimetric determination of serum cholesterol.

J. CARUSO and G. H. SCHENK

Measurement of serum cholesterol synthesis employing deuterium.

C. B. TAYLOR, B. MIKKELSON,
 J. A. ANDERSON and D. T. FORMAN

Nature of lactic dehydrogenase isoenzymes.

N. RESSLER, U. COOK, E. OLIVERO
 and R. JOSEPH

New applications of Starch gel electrophoresis to study of complex molecules.

A. L. KOEN

Determination of acid mucopolysaccharides in tissue culture.

Y. SHIMIZU and D. FRANCIS

Chromatography

Application of gas chromatography to determination of carbonate carbon in sodium metal.

H. BRADLEY, J. FERGUSON and
 S. A. MEACHAM

A modified high temperature combustion technique for determination of carbon in sodium.

Separation of methyl and propyl esters of p-hydroxybenzoic acid by gas chromatography and their determination by ultraviolet spectroscopy.

New correlations between physical properties and gas chromatographic retention times for members of various homologous series of organic compounds.

Identification of polymeric materials using two new instrument attachments.

Rapid quantitative determination of long chain tertiary amines by thin layer chromatography.

Column, paper and thin-layer chromatographic characterisation methods for aromatic compounds and their application to air pollution.

Column chromatographic separation of basic polynuclear aromatic compounds from complex mixtures.

Spectrophotometry

Precision analysis of high purity gallium by indirect spectrophotometry.

Simultaneous determination of trace amounts of titanium and zirconium.

Improved spectrophotometric method for determination of organo aluminium compounds.

Indirect spectrophotometric determination of chlorine dioxide.

Spectrophotometric determination of antimony.

Determination of oxides of nitrogen in effluent of an inert gas generator.

Method for sampling and analysis of nitrogen in potassium.

Determination of fluorine in organic compounds.

Friday Afternoon, October 23: Symposium on Automation in Analytical Chemistry

Automation in analytical chemistry.

Automated determination of proteins.

Automated determination of iron.

Kinetic measurements in the clinical laboratory.

Automatic, real time digital integration of amino acid peaks.

Automatic potentiometric EDTA and redox titrations of non-stoichiometric compounds.

Automated system for rapid and precise neutron activation analysis.

Industrial Application of Optical Methods of Analysis

Refinement of spectrochemical procedures.

Spectrographic determination of impurities in beryllium.

Industrial applications of atomic absorption spectroscopy.

Vacuum ultraviolet instrumentation and development and manufacture of a double beam monochromator for ultraviolet region.

Vacuum ultraviolet and soft X-radiation detection.

A precise recording absolute spectrofluorometer.

Optical emission spectrographic method for determination of chloride ion in chromium plating baths.

Spectrochemical determination of microgram amounts of tantalum, niobium, titanium and hafnium in U₃O₈.

E. J. HAVLENA and H. V. MYERS JR.

S. J. DONATO

B. J. GUDZINOWICZ

K. A. HUTCHINSON

J. R. PELKA and L. D. METCALFE

E. SAWICKI, H. JOHNSON and
T. W. STANLEY

E. SAWICKI, J. E. MEEKER and
M. MORGAN

R. BASTIAN, R. S. KELLY and
E. W. LANNING

J. O. HIBBITS, A. F. ROSENBERG
and R. T. WILLIAMS

S. R. HENDERSON, T. G. MUNGALL
and J. H. MITCHEN

J. A. HOWELL, G. E. LINNINGTON
and D. F. BOLTZ

J. C. GUYON and R. M. MATULIS

D. M. ZALL

H. KIRTCHIK

M. BRANDT and D. G. COBB

B. KLEIN

E. S. BAGINSKI and B. ZAK

B. ZAK

D. G. REMP

D. W. SPENCE and H. J. JONES

M. C. GARDELS and J. C. CORNWELL

J. R. VOGT and W. D. EHMANN

J. K. HURWITZ

E. S. MELICK, L. BUNCK and
E. PETERSON

R. E. MANSELL

P. M. MCPHERSON

C. F. HENDEE

G. K. TURNER and R. E. PHILLIPS

W. EDGAR and N. B. PARSEGHIAN

J. E. SCOTT and E. R. SHUSTER, JR.

Monday 30 November–Friday 4 December 1964: Short Course on Gas Chromatography: Instrument Society of America. Carnegie Institute of Technology, Pittsburgh, Pa. (see *Talanta*, 1964, 11, August iii).

New standard samples for four groups of copper-base alloys have been issued by the National Bureau of Standards Institute for Materials Research. Several samples, which vary in composition, are available for each of the alloys—free-cutting brass, gilding metal, commercial bronze and aluminium brass. These standards have been prepared primarily for optical-emission and X-ray spectrochemical analysis calibrations and are in a form convenient for such use.

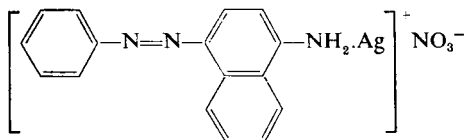
American Society for Testing and Materials has compiled the *Wyandotte-ASTM Punched Card Index* for finding and correlating infrared spectral absorption data using programmed tapes for computers. These tapes are used in connection with the Codes and Instructions for the Wyandotte-ASTM Punched Card System. This system facilitates the sorting of spectral data in matching spectrograms in qualitative analysis. Further information is available from Dr. L. E. KUENTZEL, ASTM, 1916 Race Street, Philadelphia, Pa. 19103.

American Society for Testing and Materials has announced the availability of the following publication:

ASTM Standards for Industrial Water and Atmospheric Analysis: Part 23 of 1964 Book of ASTM Standards (Price \$13.00; \$9.10 to ASTM members). This contains 98 standards of which 58 are new or have been revised since the publication of the 1960 edition of *Manual on Industrial Water-D-19*, which it replaces. The contents include industrial water—sampling and analytical methods, corrosion tests, methods of reporting; atmospheric analysis.

ERRATA—Volume 11

Page 1098: The structural formula for compound III should be



Page 1121: The title should read *Colorimetric determination of cobalt^{II}*

Page 1136, Table I: the second entry in the last column should read 0.511 MeV

Page 1137, Table II: The entries in the third column should read 0.511 MeV and 1.04 MeV

Page 1177: This paper should read *Eingegangen am 15. Februar 1964*

Page 1200, Table III: The heading to the fifth column should read *Found, 0.05M, ml*

Page 1203: This paper should read *Received 10 February 1964*

Page 1239: This paper should read *Received 18 March 1964*

Page 1249: This paper should read *Received 9 April 1964*

Page 1275: This letter should be dated 26 March 1964

Page 1284, Fig. 5: This should read $\gamma_0 = 0.06$, etc.

Page 1313, line 4 of Experimental: This should read 1,2-diaminocyclohexanetetra-

Page 1314, line 2 of Apparatus: This should read *photoelectric attachment*

Page 1314, line 8 under Results and Discussion: This should read *a molar ratio of 1:1, V:(XO)*,

Page 1325, second footnote to page: Delete *Preparation*:

Page 1329: This should read *Table 1*

Page 1350, line 14 of Results and Discussion: This should read *measured in 1-ml cells*

Page 1355, reference 6: The journal should read simply *Japan Analyst*

Page 1366, line 3 above Procedure: This should read (1 ml \equiv 100 μg of cadmium)

Page 1367, line 7 from bottom of page: This should read *chromium(VI), remaining after volatilisation, to chromium(III)*

Page 1377, line 2 under Calculations: This should read 6–7 MeV

PAPERS RECEIVED

- Analysis of ores containing lead, copper and zinc by anion-exchange chromatography and complexometry:** D. SEN GUPTA and R. N. SEN SARMA. (7 August 1964)
- Remote simultaneous titration of free acid and metal ions in irradiated fuel re-processing solutions:** H. H. PH. MOEKEN, H. KEESE and W. HEINZ. (10 August 1964)
- The methoxyl content of *Acacia* gum exudates:** D. M. W. ANDERSON, G. M. CREE, M. A. HERBICH, K. A. KARMALLA and J. F. STODDART. (10 August 1964)
- Precipitation of copper 8-hydroxyquinolate from homogeneous solution:** R. P. GRAHAM, E. J. BILLO and J. A. THOMSON. (14 August 1964)
- Selektive Trennung von Selen(IV) durch Extraktion mit Methyläthylketon:** N. JORDANOV und L. FUTEKOV. (17 August 1964)
- Spectrophotometric investigation of the nature and stability of silver(II) in acidic sulphate media:** G. A. RECHNITZ and S. B. ZAMOCHNICK. (17 August 1964)
- Applications of precipitate membranes in analytical chemistry:** T. BRAUN and J. TÖLGYESSY. (18 August 1964)
- Complexes of 3-methylgalangin with uranyl and thorium ions:** MOHAN KATYAL and R. P. SINGH. (19 August 1964)
- Theoretical considerations in the zone melting of organic substances:** PAUL J. JANNKE and ROBERT FRIEDENBERG. (21 August 1964)
- Selective retention of alkali metals on cation-exchange resin: Rapid separation of alkali metals from other metals:** EUGENE D. OLSEN and HAROLD R. SOBEL. (17 August 1964)
- Relation between the shapes of titration curves of a dibasic acid and of a mixture of two monobasic acids with equal concentrations:** A. A. BUGAEVSKY. (22 August 1964)
- Spectrophotometric study of the iron(III) reaction with 3,5-di-iodine-salicylic acid and its utilisation in iron determination:** I. C. CIUREA, GR. POPA and C. LAZAR. (1 September 1964)
- Selective spot tests for glyoxal, pyruvic and lactic acid:** F. FEIGL and S. YARIV. (2 September 1964)
- Application of steady-state controlled-potential coulometry to the study of homogeneous solution reactions:** G. A. RECHNITZ and J. E. MCCLURE. (2 September 1964)
- Eine Analysemethode des nichtwässrigen Medium: Die Bestimmung von aromatischen Aminen:** LÁSZLÓ LÉGRÁDI. (2 September 1964)

PUBLICATIONS RECEIVED

Chromatographie Symposium II, 1962: Société Belge des Sciences Pharmaceutiques, Rue Archimède, 11, Bruxelles 4, Belgium. 1963, pp. 310. 150 B.F.

Papers presented at the Second Symposium on Chromatography, held in Brussels 14-15 September, 1962 by the Belgian Society of Pharmaceutical Sciences.

Conferences: Chromatographie sur papier et en couche mince des alcaloïdes et des flavonoïdes: Récentes acquisitions sur l'identification chromatographique des oses et oligosaccharides: Polyamidchromatographie: Gas-liquid chromatography: a compact gas-radio chromatogram.

Communications: Les procédés d'étude de la structure des glycoprotéides: Sur la séparation chromatographique sur papier des ions; magnésium, calcium, sodium et potassium; applications aux eaux minérales: Dünnschicht-verteilungschromatographie der Plastidenpigmente: Concernant la séparation des amino-acides par chromatographie en phase gazeuse: Chromatographie des acides désoxyribonucléiques sur papier de diéthylaminoéthyl-cellulose: Chromatography and electrochromatography of gastric and duodenal extracts: The detection of lipoproteins after electrochromatography: Étude chromatographique de dérivés substitués du lysozyme: Étude comparative des hémoglobines humaine, de lapin et de poule: Fractionnement des protéines soluble du jaune d'oeuf de poule: Dünnschichtchromatographie von Tricarbonsäurezyklus-substraten mit Autoradiographie: Radiochromatographie sur Dowex des acides aminés iodés du sérum: Chromatographic separation of the components of staphylomycin: Considérations sur l'analyse chromatographique des sulphamides: Papierchromatographische Trennung der gebräuchlichen Kationen: Chromatography of Doriden (α -phenyl- α -ethyl glutarimide) in postmortem material on coated glass sheets: Die Dünnschicht-Chromatographie als Analysenmethode zur Untersuchung lipophiler sekundärer Pflanzeninhaltsstoffe unter besonderer Berücksichtigung der Harze und Balsame: Recherches chromatographiques sur les acides aminés libres des vins naturels: Chromatographie de flavonoïdes sur échangeurs d'ions: Dünnschichtchromatographie von Phosphatiden, Glykolipiden und Ubicenonen: Chromatographie sur verre sablé et muni de couches minces: Utilisation de la poudre de verre en chromatographie sur couche mince: The Unikit: an apparatus and Manual for the teaching of chromatography and electrophoresis on paper: The adsorption system in column and thin-layer chromatography; recent results: Les applications de l'automatisme à la séparation chromatographique et au dosage des acides aminés, peptides et protéines: Spectrofluorimetric identification of chromatographically separated plastid pigments: Les cétoles de l'urine: Chromatographie des protéines urinaires: Fractionnement chromatographique des hétérosaccharides du colostrum humain: The biosynthesis of unsaturated fatty acids in plant systems: Dünnschichtchromatographie von Phloroglucinbutanonen:

Immunochemistry: Vol. I, No. 1, April 1964. Regional Editors: DAN H. CAMPBELL, ALAIN BUSSARD, HENRI ISLIKER, FRED KARUSH. Pergamon Press, Oxford, London, New York, Paris, quarterly, pp. 63. Annual subscription rates: (A) For libraries, government establishments, research institutions, etc., £15 (\$40.00): (B) For individuals who place their orders directly with the publisher and certify that the Journal is for their personal use, £5 (\$15.00).

J. F. GERSTEIN, L. LEVINE and H. VAN VUNAKIS: Altered antigenicity of pepsinogen and pepsin as an index of conformational change: effect of urea and reducing agents. S. J. SINGER: On the heterogeneity of anti-hapten antibodies. M. EICHLIN, M. HOY and L. LEVINE: Antibodies to human A₁ hemoglobin and their reaction with A₂, S, C, and H hemoglobins. J. L. GROFF and F. HAUROWITZ: Comparison of the peptide maps of antibodies against an acidic and basic determinant group. P. J. LACHMANN and C. B. RICHARDS: Some molecular parameters of bovine conglutinin. L. GYENES and A. H. SEHON: The use of tolylene-2,4-diisocyanate as a coupling reagent in the passive hemagglutination reaction. F. FRANĚK and I. ŘIHA: Purification and structural characterization of 5 S γ -globulin in new-born pigs.

Application of Distillation Techniques to Radiochemical Separations: JAMES R. DEVOE, National Academy of Sciences, National Research Council, Nuclear Science Series, Radiochemical Techniques. NAS-NS 3108, Aug., 1962. Pp. 29, \$0.50. (Available from the Office of Technical Services, Department of Commerce, Washington, 25, D.C., U.S.A.)

Introduction: The Distillation Process for Radiochemical Separations: Radiochemical Distillation Procedures; Hydrogen; Rare Gases; Carbon, Nitrogen and Oxygen; Halogens; Alkali Metals; Silicon; Phosphorus; Sulfur; Alkaline Earths, Rare Earths and Yttrium; Vanadium; Chromium; Manganese; Germanium, Arsenic, Antimony and Tin; Selenium and Tellurium; Ruthenium, Osmium, Technetium, Rhenium; Rhodium and Silver; Cadmium; Indium; Gold; Mercury; Lead; Bismuth; Polonium; Astatine; Uranium: References (66).

Interpretation of Mass Spectra of Organic Compounds: HERBERT BUDZIKIEWICZ, CARL DJERASSI and DUDLEY H. WILLIAMS. Holden-Day, Inc., San Francisco, U.S.A., pp. xiii + 271, 1964, \$8.75.

Aliphatic and monocyclic carbonyl compounds: Alcohols: Ethers, thioethers and mercaptans: Amines and amides: Cyclic amines: Aliphatic cyanides and isothiocyanates: Alkyl halides: Bicyclic ketones: Aromatic hydrocarbons and functional derivatives: Tropones and tropolones: Aromatic heterocyclics: Index.

Controlled Potential Analysis: GARRY A. RECHNITZ. International Series of Monographs on Analytical Chemistry, Volume 13. Pergamon Press. Ltd., Oxford, London, New York, 1963, pp. 85, 35s.

Introduction: Theory: Apparatus and Techniques: Analytical Applications: Author Index: Subject Index.

Titrimetric Organic Analysis, Part I: Direct Methods. M. R. F. ASHWORTH. (Chemical Analysis, Volume 15, Editors, P. J. ELVING and I. M. KOLTHOFF.) Interscience Publishers (John Wiley and Sons) New York, London, Sydney, Pp. xx + 501, 132s.

Introduction: *Section 1*; Titration Procedure; Physical properties and measurements in end-point determination: (A) Light absorption, (B) Electrical properties, (C) Temperature, (D) Other physical properties; Automatic titration; Reactions used in the direct titration of organic compounds; Examples of direct titration of organic compounds: *Section 2*; Reagents (117 categories) used in direct titration of organic compounds: *Section 3*; Index to functional groups and compound classes (105 entries): Indexes.

Handbuch der Kolorimetrie, Band II: Kolorimetrie in der Pharmazie: BOHUMIL KAKAČ and ZDENĚK J. VEJDELEK. Übersetzt von E. HACHOVÁ. VEB Gustav Fischer Verlag, Jena, DDR., 1963, pp. xv + 1128, £7 1s. 0d.

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II. Organopreparate

III. Steroide

IV. Einige anorganische anionen.

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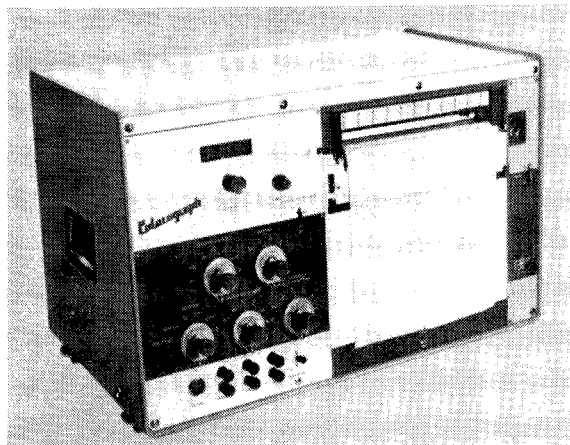
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CONTENTS

A. PÁLL, G. SVEHLA and L. ERDEY: Determination of cobalt(II) ions by a differential spectrophotometric method	1383
TSUGIO TAKEUCHI and MASAMI SUZUKI: The determination of sodium, potassium, magnesium, manganese and calcium in cement by atomic-absorption spectrophotometry	1391
H. LOEWENSCHUSS and G. SCHMUCKLER: Chelating properties of the chelating ion exchanger Dowex A-1	1399
C. P. LLOYD and W. F. PICKERING: A study of the oxidation of manganese(II) and chromium(III) ions by silver(II) oxide	1409
PAUL D. GARN: Some problems in the analysis of gaseous decomposition products: A critical evaluation	1417
E. SAWICKI, T. W. STANLEY and W. C. ELBERT: Quenchofluorometric analysis for fluoranthenic hydrocarbons in the presence of other types of aromatic hydrocarbon	1433
JAMES O. HIBBITS and SILVE KALLMANN: Some rather unusual chemical analyses	1443
K. C. AGRAWAL and F. E. BEAMISH: Studies of the fire assay for platinum metals by lead collection	1449
Short communications	
ANTONI BAŚŃSKI and KAZIMIERZ KICIAK: A new class of fluorescent adsorption indicators	1459
TÔRU MEKADA, KÔICHI YAMAGUCHI and KEIHEI UENO: Use of masking agents in chelatometric titrations—IV: Dimercaptosuccinic acid	1461
JAMES O. HIBBITS, SILVE KALLMANN, WILLIAM GIUSTETTI and HANS K. OBERTHIN: A specific method for the determination of trace amounts of titanium	1464
G. A. RECHNITZ: Response rates of cation-sensitive glass electrodes	1467
Letter to the Editor	
R. PŘIBIL: The international nature of TALANTA	1469
Notices	i
Papers received	vi
Publications received	vii