

An International Journal of Analytical Chemistry

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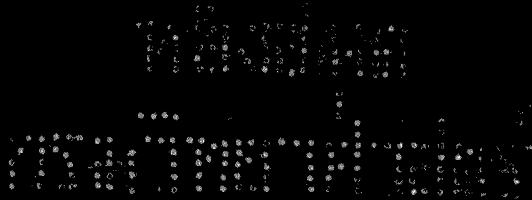
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# Talanta

An International Journal of Analytical Chemistry



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# TALANTA MEDAL



DR. ALAN WALSH

The Editorial Board of *Talanta* has pleasure in announcing that, with the approval of the Advisory Board, The Fifth Award of the Talanta Medal (see *Talanta*, 1966, **13**, 1052) has been made to

DR. ALAN WALSH

of the Department of Chemical Physics, C.S.I.R.O., Melbourne, Australia.

The evolution of Atomic-Absorption Spectroscopy is due to the efforts and skill of Dr. Walsh. This technique has completely revolutionized the scene in trace analysis in analytical chemistry and is used extensively throughout the world. The method provides a "lock and key" means for the determination of metals, simply by spraying solutions of metal salts into a flame where free atoms are produced. Walsh's contribution to the technique arises from his development of the hollow-cathode lamp, which made possible the technique as we know it today. The free atoms in the flame attenuate the signal from the corresponding hollow-cathode lamp, and the spectral width of the absorption lines is so narrow that spectroscopic interference is only rarely observed. In simplicity and cost the technique challenges strongly the other methods of trace analysis for metals. It also has the advantage that by various indirect methods it can be used for the trace determination of non-metals and specific compounds.

## TALANTA REVIEW\*

### APPLICATIONS OF DIGITAL COMPUTERS IN ANALYTICAL CHEMISTRY—I

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**Summary**—Digital computers are currently applied to a wide range of chemical problems. Aspects of particular interest to analytical chemists, including statistical treatment, X-ray analysis, spectroscopy, mass spectrometry, gas chromatography and electroanalytical chemistry, are discussed.

THE MATHEMATICAL treatment of experimental results in chemistry has been greatly aided by the development of electronic digital computers with adequate storage capacities and very fast computing times. The present Review discusses applications of computers to problems of interest to analytical chemists.<sup>1</sup> We have not tried to cover all papers which deal with the use of computers but have selected representative examples which illustrate their applications. Topics such as force constant calculations from infrared studies, and Hückel molecular orbital calculations, lie outside the scope of this Review.

Only a few applications of analogue computers (in which suitable physical quantities such as electrical voltages are used to represent the variables in the problems to be solved) have been included, because these devices lack the flexibility, accuracy, storage capacity and programming ability of modern digital computers and they appear to have very limited use in analytical chemistry.

The simplest and most common use for a computer is as a replacement for a desk calculator in long, complex or repetitive calculations required to convert physical measurements into desired quantities. The data may be taken by an operator and manually punched on to cards or paper tape for subsequent computer analysis, but an improvement, especially where large volumes of data are involved, is the automatic conversion of the physical measurement into a suitable digital form. This is carried out by some form of analogue-to-digital converter attached to the measuring instrument and the digital output is punched on to cards or paper tape, recorded on magnetic tape, or fed directly to the computer for analysis. The time saved by automatic data punching can be significant, but the main advantage is the elimination of human error in data transcription.

A further development is the display, on a cathode-ray tube attached to the computer, of the raw or partially processed data existing in the computer storage. This allows the operator to combine his judgment with the facilities of the computer,

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usually in rejecting or reserving data for subsequent storage or processing. Such a system can decrease the inessential processing often carried out by a computer on a particular problem and can also reduce the possibility of processing faulty data. In some cases, computer output is applied to control apparatus or equipment.<sup>2</sup>

The advent of high-speed automatic computers permits more complicated calculations to be made than were previously possible. Theoretical models that were previously limited to simple linear functions can be expanded to include several parameters which are adjusted to fit experimental observations. The same kinds of mathematical treatment are relevant to diverse chemical problems, so that a generalization of the Newton-Raphson<sup>3</sup> method for  $m$  functions of  $n$  variables is applied, for example, to curve-fitting of ultraviolet spectra,<sup>4</sup> electron spin resonance curves<sup>5</sup> and Mössbauer spectra.<sup>6</sup> Many of the computational problems encountered in spectrophotometry also occur in atomic absorption, electron spin resonance, and gas chromatography.

The programming of computers has been greatly facilitated by the development of convenient computer languages, such as FORTRAN<sup>7</sup> and ALGOL<sup>8</sup> for scientific purposes and COBOL for commercial transactions. Mathematical procedures especially suited to computers are also available,<sup>9</sup> and many of the more commonly required ones have been prepared as subroutines (small self-contained programmes) for incorporation in computer programmes. It is important, when using a digital computer, to foresee logical contingencies and include them in the instructions that constitute the programme.

Applications of computers to automation and process control in the chemical industry have been reviewed elsewhere.<sup>10</sup> Typically, transducers or converters are used for sensing the experimental conditions, while a computer programme gives instructions for recording the results and initiates new settings of the apparatus. These techniques can readily be adapted to the large scale needed for the control of chemical plant.

#### ERROR ANALYSIS AND STATISTICAL TREATMENTS

To assess the reliability of his experimental results or their closeness of fit to some specified relation, the analyst may use a wide range of statistical methods. He might calculate quantities such as the mean, and the standard deviation (root mean square deviation) from the mean. He might apply Student's  $t$ -test to compare two means, or a least-squares method to fit the best straight line, or some other relation, to the experimental data. All of these operations are highly suitable for digital computer programming.

A simple programme has been described<sup>11</sup> for introducing students to the computer evaluation of errors in analysis. A mixture containing, for example, ammonium chloride and ammonium sulphate, was analysed chemically and the results were used to compute composition, standard deviation of the mean, observed probable error of weighted mean, and the theoretical error of the weighted mean.

Gottschalk<sup>12-15</sup> has made a detailed study of electronic computing for the statistical treatment of analytical results. In Part I in his series a computer programme is described for evaluating an analytical method by statistical analysis (mean, standard deviation, coefficient of variation) of results from a series of model experiments.<sup>12</sup> Worked examples were for chloride estimation by Mohr's method, and the gravimetric determination of tungsten by 8-hydroxyquinoline. In Part II, a programme is given

for testing the homogeneity between groups of data by a simple analysis of variance: the *t*-test proposed by Nalimov<sup>16</sup> also enables the homogeneity of single values in each group to be assessed.<sup>13</sup> As an example, results obtained by seven laboratories for the flame-photometric determination of sodium in a homogeneous glass sample were compared. Subroutines are also given for checking (by statistical methods for interpreting correlations) the relationship between variable experimental parameters for similar objects or processes,<sup>14</sup> and these are incorporated into a computer programme for the least squares adjustment of systematically varied functions to obtain the relationship between different sets of experimental data.<sup>15</sup> The programme was tested with results for sodium and potassium determinations by flame photometry at concentrations where non-linear calibration was found.<sup>15</sup>

Much experimental work yields results of a two-column tabular nature (*e.g.*, pH *vs.* volume of titrant, polarographic current *vs.* applied voltage, absorbance *vs.* wavelength) in which random errors are superimposed on the quantities being measured. The effect of random errors is reduced if data obtained at uniform intervals (of volume, voltage, wavelength, *etc.*) are convoluted by using an appropriate smoothing function. This is achieved by taking a small number of consecutive points at a time, preferably very close together and not containing more than one maximum, minimum or inflexion. A least-squares computer programme for carrying out this smoothing has been described,<sup>17</sup> based on the use of a polynomial of degree *n* with properly chosen sets of integers (which are tabulated for steps of 5–25 points, for polynomials up to the fifth degree). The technique is applicable to all types of curves, obtained either manually or mechanically. It has been used, for example, to locate peaks and obtain peak areas and peak energy measurements in scintillation spectrometry.<sup>18,19</sup>

Monte Carlo methods (discussed in Part II) are based on the technique of random sampling. They are useful for solving some kinds of problems for which conventional mathematical methods are unsatisfactory. Fluendy and Smith<sup>20</sup> have reviewed the application of Monte Carlo methods to physicochemical problems where, typically, they provide useful mathematical simulations of physical systems for studying phenomena such as order-disorder, configuration of macromolecules, or properties of dense phases. These methods are readily programmed for use with large digital computers, and they can be applied to problems which could be solved numerically only with considerable difficulty or which are statistical in nature and lack explicit mathematical forms.

#### MOLECULAR STRUCTURE DETERMINATION BY X-RAY DIFFRACTION

The earliest applications of computers to chemical research were in crystal structure determinations by X-ray diffraction. In 1952, Bennett and Kendrew<sup>21</sup> described programmes for computing Patterson and Fourier syntheses in two and three dimensions with EDSAC (the Cambridge University's Electronic Delay Storage Automatic Calculator), and Ahmed and Cruickshank<sup>22</sup> refined the structures of naphthalene and anthracene by using the Manchester University's electronic digital computer which had begun operation the previous year. Wheatley<sup>23</sup> used the same computer in work on ethylenethiourea. By present standards these machines were slow and of very limited storage capacity, and programming in binary machine language was tedious. Nevertheless, they were a major advance on previously available techniques



using desk calculating machines, Hollerith punched-card methods and analogue-type apparatus. Since then the development of powerful computers, together with the application of the heavy-atom isomorphous replacement technique, has made it possible to determine structures previously too complex for elucidation. Examples of these include the macromolecules lysozyme,<sup>24</sup> myoglobin,<sup>25</sup> papain,<sup>26</sup> and horse haemoglobin.<sup>27</sup>

Because most of the extensive mathematical operations used in the treatment of crystallographic data are independent of the nature of the crystal being studied, there has been considerable development of general computer programmes for these purposes. Many of these programmes have been published, and a compilation of some of them is available.<sup>28</sup> Another useful literature source is "Computing Methods in Crystallography."<sup>29</sup> Nevertheless many crystallographers still prefer to write their own routine programmes.

Determination of crystal structures by X-ray diffraction frequently requires the measurement of integrated reflexions of thousands of spots on a photograph. This has stimulated efforts to develop automatic devices for recording such data. For example, Abrahamsson<sup>30</sup> built a computer-controlled film scanner for X-ray work which measured intensities at every point on an 0.1-mm grid covering the whole film and stored the information magnetically for subsequent computation. Frevel<sup>31</sup> has described a system which converts digitized film data from a precision microphotometer into a computer-controlled print-out of interplanar spacings and peak intensities. An approach requiring much less computer capacity is due to Wooster<sup>32</sup> who pointed out how an instrument can be programmed to find the co-ordinates of each spot on a film and to compute the indices of the reflecting plane.

He suggested that, alternatively, the co-ordinates of spots on films could be computed so that a microdensitometer, with automatic setting along two mutually perpendicular directions, could set the film in the required positions for subsequent measurement.

With the advent of bigger and faster computers, the computational problems of X-ray crystallography have diminished in relative importance and the quality of structural determination work is becoming limited by the experimental measurements themselves. These can be improved by the computer-controlled application to the experimental results of such factors as Lorentz and polarization corrections,<sup>33</sup> allowances for spot shape and non-linear photographic response, and correction for background absorption. With improvements in computing techniques, programmes have become more general and flexible.<sup>34</sup> The input data might include provision for the crystal class to be specified by a single number and the full space group by its symbol from the International Tables.<sup>35</sup> With this information, the computer could be directed to the parts of a programme appropriate to the type of crystal being studied.

Automatic graph-plotting of electron density contours is now feasible, and programmes are available for recording them by pen-type plotter,<sup>36,37</sup> or for presenting them on a cathode-ray tube plotter attached to a small computer.<sup>38</sup> Application of neutron diffraction techniques to locate the positions of hydrogen atoms is extending information from X-ray diffraction studies.

By reducing the arithmetical labour and manual effort in data processing, computers have facilitated analytical applications of X-ray diffraction techniques. A

computer programme has enabled identification to be made of crystalline phases in powdered samples by a search-and-match procedure<sup>39</sup> on powder diffraction data and elemental analysis. Other programmes have been described for indexing X-ray powder patterns<sup>40-43</sup> and for correcting for interelemental effects in the X-ray spectrochemical analysis of silicates.<sup>44</sup> The latter programme determines the coefficients needed to correct for interelemental absorption and enhancement effects.

#### ELECTRON PROBE MICROANALYSIS<sup>45</sup>

In a computer programme for quantitative and semiquantitative analysis with the electron microprobe analyser, the weight fraction of each element in the specimen is determined from the characteristic X-ray intensity measurements of the specimen and of the standards.<sup>46</sup> Another programme calculates the relative characteristic X-ray intensities for all elements in a specimen, assuming its composition to be known.<sup>46</sup> Corrections are applied by the computer for dead-time, background (which may be constant or dependent on composition), absorption, fluorescence and composition. An alternative approach is to supply the X-ray intensities from sample and standards to a computer which applies appropriate corrections, and refines, iteratively, the initial estimates of composition until the best fit is obtained between observed and computed spectra.<sup>47</sup>

#### SPECTROSCOPY

Computer techniques have assisted in a number of problems common to many branches of spectroscopy. Foremost among these is the detection and resolution of overlapping peaks. Most of the programmes described have been written to determine infrared parameters (frequency, intensity and half-band width) and nuclear magnetic resonance parameters (chemical shifts and coupling constants), but Fraser and Suzuki<sup>48</sup> have demonstrated the general application of band resolution by applying it to the output of an amino-acid analyser, to the trace of the equatorial distribution of intensity in an X-ray diffraction pattern and to a polarized infrared spectrum,

General methods of band resolution are based on the approximation of unperturbed bands by analytical functions which may be either Gauss or Lorentz band shape functions or sum and product combinations of these two.<sup>49</sup> The method outlined by Stone<sup>50</sup> is based on an iterative least-squares method and assumes that each spectral line has the same general shape (either Gaussian or Lorentzian). Another programme,<sup>51</sup> based on this method, uses the Levenberg method of damped least-squares which is claimed to give more rapid convergence than the method of steepest descent employed by Stone.<sup>50</sup>

For the analysis of electronic absorption spectra, Roos<sup>4</sup> described a similar programme which assumes Gaussian band shapes. In an analysis of errors which arise in separating overlapping bands, Morrey<sup>51a</sup> used a computer, first to generate a spectrum from ten Lorentzian frequency functions chosen to give a variety of overlapping peaks, and then to analyse the spectrum. When the data were digitized at  $10\text{-cm}^{-1}$  intervals, nine of the ten peaks were successfully determined and the maximum difference between the computed transition energies and the values used to generate the spectrum was  $1.4\text{ cm}^{-1}$ . The method is capable of accurately locating peaks which appear only as shoulders on stronger peaks. A detailed comparison has been made of seven numerical methods of fitting infrared band envelopes with analytical functions by using non-linear least-squares approximations.<sup>49</sup> With digital computers it is

possible to generate analytical expressions that will fit the contours of the infrared band envelopes with a precision approaching that of the statistical uncertainty of the measurements.<sup>49</sup> The indices of these analytical expressions may provide a much more economical way of handling and storing total high resolution infrared spectra for subsequent computer search, than do intensity and frequency data over the whole range of the spectrum.<sup>52</sup> For satisfactory spectrum retrieval, with this latter method, the spectrum must be digitized at maximum intervals of  $0.5\text{ cm}^{-1}$  and for a full spectrum, covering the range  $4000\text{--}300\text{ cm}^{-1}$ , 14800 frequency and intensity values are necessary. Such voluminous data present handling and storage difficulties. Present methods of storing infrared spectra are therefore limited to a record of the positions of peaks and some chemical information: the use of a total infrared spectrum is a logical extension.

Anderson and Covert<sup>53</sup> have written a programme which searches the ASTM file and compares up to five unknown spectra with the standard spectra at a rate of about 10000/min. Each unknown spectrum is fed into the computer as a series of peak positions, including a listing of peak-free regions, together with known chemical information and the melting or boiling point. The computer compares this information with that stored on disc or tape and matching or nearly matching spectra are specified in the computer output. A similar programme has been designed for a small computer to be operated by the spectroscopist: input of data is through the computer console rather than by the more usual means of punched cards or tape.<sup>54</sup>

Reid and Wong<sup>55</sup> have discussed the problem of digitizing and recording ultraviolet and visible spectra for subsequent computer search routines. The whole spectrum is digitized and stored at 1-nm intervals and an unknown spectrum is compared with the standards and a correlation coefficient is calculated. Values of this coefficient range from 0 to 1, with 1 representing a perfect match. Spectra with coefficients greater than a specified value (*e.g.*, 0.995) are listed for the operator's attention. This technique of comparing the whole spectrum is essential for ultraviolet and visible spectra where bands are broad and lack the fine structure associated with infrared spectra.<sup>55</sup>

Commercial equipment is now available for digitizing instrument outputs from ultraviolet, infrared and atomic absorption spectrophotometers in ways suitable for computer processing either at some central facility or directly in a small, local instrument. One such system comprises an analogue-to-digital converter, with facilities for peak detection, offset and scaling, timing and counting. Refinements include display, manual entry and instrument control. Computer programmes cover analysis of mixtures, encoding of spectra, identification of library spectra, analysis of line shape, time averaging, integration, correction for baseline shift, digital smoothing, and peak triggering and offset.

A more unusual application is the use of computers of average transients (CATs) for the improvement of signal-to-noise ratios. Successive rapid scans of the spectrum of interest are averaged so that random positive and negative noise components tend to cancel. The improvement in signal-to-noise ratio is by a factor of  $N^{\frac{1}{2}}$ , where  $N$  is the number of scans summed. The CAT is ordinarily applied to NMR and ESR spectra<sup>56-58</sup> but it has been successfully used in other fields of spectroscopy.<sup>59,60</sup> An alternative computer method for improving spectra is the least-squares convolution method described by Savitzky and Golay<sup>17</sup> which uses a computer as a filter to smooth

noise fluctuations without introducing appreciable distortions in the recorded data such as result from moving average or similar convolute functions. On the other hand, distortion due to finite spectral slitwidths has been allowed for in a computer method termed "pseudo deconvolution."<sup>61,62</sup> The reported gain in resolution was equal to that obtained by halving the spectral slitwidth.<sup>61,62</sup> The method avoids the diminution in signal-to-noise ratio which is associated with a decrease in slitwidth.<sup>61,62</sup>

The determination of component concentrations from the spectrum of a mixture has been dealt with by several authors.<sup>63-65</sup> Provided the spectra of the pure components are known, the computer can be programmed to calculate the concentration of each component in the mixture. The programme described by Blackburn can handle up to 20 component spectra and was written for application to  $\gamma$ -ray spectrometry;<sup>63</sup> DeTar<sup>64</sup> applied his programme to infrared measurements and Mandeles and Cantor<sup>65</sup> investigated the ultraviolet spectra of nucleic acid oligomers.

The use of computers to obtain stability constants from spectroscopic measurements is discussed in Part II of this Review.

Major developments can be expected in the applications of computers to spectrochemical systems. Hasler<sup>66</sup> has discussed current examples involving optical emission, X-ray fluorescence and electron microprobe techniques.

### *Nuclear magnetic resonance*

Computers have been widely used in the interpretation of nuclear magnetic resonance (NMR) data. Their most common application, which is one of great interest in analytical chemistry, is in the analysis of complex high-resolution spectra to give the magnetic parameters (chemical shift and coupling constant) but computers have also been used to advantage in chemical exchange studies. A detailed review<sup>67</sup> deals with the application of computers to both problems. Another review<sup>68</sup> is limited to the determination of the magnetic parameters from high-resolution studies. Both of these quote programmes which are frequently used in NMR calculations.

Programmes for the analysis of high-resolution spectra include those developed by Swalen and Reilly<sup>69</sup> (NMRIT, NMREN and NMRPLOT) and a later modification,<sup>70</sup> by Bothner-By and co-workers<sup>71-74</sup> (LAOCOON and FREQUINT), and by others.<sup>75-80</sup> Swalen also catalogued the problems dealt with by the more commonly used programmes.<sup>67</sup>

The simplest approach to the problems of resolving a complex NMR spectrum into its magnetic parameters is by trial-and-error. Programmes are available which calculate a theoretical spectrum (line position and intensity) given values for chemical shift and coupling constant<sup>71,76-78</sup> and the trial parameters are adjusted by the operator to achieve agreement between the calculated and the observed spectrum. Wiberg and Nist have published sets of spectra calculated in this way for AB, AB<sub>2</sub>, ABC, AB<sub>3</sub>, A<sub>2</sub>B<sub>2</sub>, AB<sub>4</sub> and A<sub>2</sub>B<sub>3</sub> systems.<sup>78</sup>

This trial-and-error approach is avoided in a programme for calculating coupling constants and chemical shifts directly from the observed spectrum, but this method is limited in its application to essentially 3-spin systems.<sup>79</sup>

Where higher spin systems are encountered, an iterative approach has been successfully applied, using a computer to adjust the input parameters to match the computed and observed spectra. This can be achieved with the programmes NMREN,<sup>69</sup> NMRIT,<sup>69</sup> and LAOCOON,<sup>73</sup> among others. Swalen and Reilly<sup>69</sup> use

NMREN to calculate the experimental energy levels (and errors) from the observed spectrum, and NMRIT to calculate the energy levels from a set of trial parameters; the computer then iterates to obtain a better agreement with the experimental energy levels by altering the trial parameters. The theoretical spectrum is calculated from the final values of the parameters and is listed as line centre frequencies and intensities. NMRPLOT<sup>69</sup> is an additional programme which allows line shape to be considered, and the calculated spectrum can be traced out on a recorder for comparison with the observed spectrum. The programme LAOCOON<sup>73</sup> is capable of analysing up to and including a seven spin system. This is another iterative programme in which calculated and observed spectra are matched and trial parameters are adjusted by a least-squares procedure.

Although these programmes are satisfactory for the analysis of a wide range of observed spectra (see appendix in ref.67), difficulty has been encountered<sup>80</sup> in applying NMRIT and NMREN to the analysis of 4-membered ring systems. This was attributed to the lack of suitable estimates of the NMR parameters required as input data. Two programmes (ASSIGN and DECOMP) were therefore developed<sup>80</sup> and used in association with NMRIT and NMREN.<sup>69</sup> An analysis carried out in this way did not require estimates of the magnetic parameters. The frequencies and intensities of all lines in an unresolved multiplet were determined to a large extent by DECOMP, and ASSIGN found the possible sets of energy levels which were consistent with the observed frequencies and intensities. NMREN and NMRIT were then used to calculate, for each set of energy levels, the corresponding real coupling constants and chemical shifts. In the analysis of 3-chlorothietane, three sets of energy levels were found to be consistent with the intensities and frequencies determined by DECOMP but only one set converged with NMRIT and this set gave magnetic parameters consistent with the observed spectrum.<sup>80</sup>

Various NMR techniques have been used for the study of the rates of inter- and intra-molecular exchange reactions where the rates range from 1 to  $10^6 \text{ sec}^{-1}$ .<sup>81</sup> The two most common approaches to this problem (high resolution and spin echo methods) have been critically considered<sup>82</sup> and the use of a computer is advised if mathematical accuracy is to be retained and erroneous simplification is to be avoided.

A study of the line shape of an NMR peak can lead to rate constants for exchange reactions. As in the analysis of high-resolution spectra, the simplest approach to the problem is the visual comparison of experimental spectra with line shapes computed for a range of exchange rates<sup>83</sup> but a more satisfactory approach is the use of a computer to fit the observed line shape. A typical programme, CURVE 4, has been described,<sup>81</sup> together with details of the necessary input data. These include an estimate of the value of the exchange rate. The computer then alters this value to obtain a minimum in the sum of the squared deviations between the experimental and calculated line shapes. Some of the problems investigated with various computer programmes have been catalogued,<sup>67</sup> together with a detailed description of the mathematical methods available for this type of analysis.<sup>67</sup>

#### *Emission spectrophotometry and atomic absorption*

Emission spectra may be photographed or the intensities may be determined directly by photoelectric cells; the characteristics of the two methods of data collection have been discussed with reference to data reduction with a digital computer.<sup>84</sup> At present,

most workers employ photographically recorded spectra, and automatic microphotometers can be used to supply the data in digital form for computer processing.<sup>85,86</sup> One<sup>86</sup> of the computer programmes<sup>85,86</sup> for data reduction directs the computer in smoothing data, locating line functions, calculating standard deviations, and converting microphotometer readings into relative intensities.

A digital computer has been used with an emission spectrometer to determine the composition of some steels.<sup>87</sup> A mathematical relationship between the composition and the intensities of the spectral lines permitted corrections for overlapping and matrix effects. The computer also aided the calibration of the instrument.

In the spectrochemical analysis of the metal composition of red blood cells, a computer was used to convert instrument readings into elemental concentrations, to calculate the amount of each constituent per cell and per unit volume of water, and to perform a detailed statistical analysis of the results.<sup>88</sup>

Other examples of the use of computers in handling spectrochemical data are available.<sup>89-93</sup> Possible developments in spectrochemistry with the increasing use of computers have been discussed.<sup>94</sup>

An advantage of emission and absorption flame-spectrophotometry, which are common instrumental techniques in industrial analysis, is their rapidity. The averaging, transforming and interpolating of the large numbers of readings obtained, and the calculating of sensitivity values are readily accomplished by a computer, thereby decreasing human error and saving time. Several typical problems have been discussed and computer programmes and corresponding outputs described.<sup>95</sup> Extensions involving a larger computer have been made, and illustrated with examples from atomic-absorption analysis.<sup>96</sup> The computer can also construct three-dimensional curves to show, for example, the variation of absorbance and concentration with flame profile, lamp current or slitwidth.<sup>97</sup>

An oscilloscope has been used on-line with a computer, allowing the operator to delete data, restore data, fit smooth curves to the data, rotate and adjust three-dimensional axes and examine multiple sets of data, before storage or processing.<sup>96,97</sup>

Readings from standard solutions may be fitted to a second- or third-order least-squares equation which relates absorbance to concentration and which, combined with appropriate sample weights and dilution factors, converts readings into concentrations.<sup>98</sup>

### *Gamma-ray spectroscopy*

In this technique, a sample is irradiated, for example with neutrons, and the resulting gamma-ray decay spectrum permits quantitative analysis of the sample. Ideally, the spectrum should be a linear combination of the standard spectra of the components of the sample. This is only approximately true of an observed spectrum, because of experimental uncertainties. Five kinds of method have been used for the computer resolution of such spectra.

- (i) Spectrum stripping, with amplitude analysis.
- (ii) Peak resolution without stripping.
- (iii) Solution of sets of simultaneous equations.
- (iv) Curve fitting by least-squares, including weighting.

- (v) Combined statistical and least-squares analysis, with stepwise multiple linear regression.

A computer programme has been described which optimizes a linear function of many variables, which are subject to linear inequalities, to fit the observed spectrum for a mixture of elements, the individual spectra being known.<sup>99</sup> Silicon has been determined in a similar way by a linear least-squares programme with a gain shift subroutine which located the position of a reference peak in sample and standard, matching them.<sup>100</sup> Other least-squares methods have been published,<sup>101,102</sup> and one of these<sup>102</sup> also corrects for background, counting-time, decay, dead-time, and for gain and threshold shifts. Choy and Schmitt,<sup>103</sup> and Yule<sup>104</sup> used peak area methods, and another programme<sup>105</sup> was based on peak heights. Spectrum "stripping" methods have been described.<sup>106,107</sup> A feature of one such programme<sup>107</sup> is the provision for bringing the abscissae of experimental and computed curves into the same scale. Blackburn<sup>108</sup> has examined this aspect in more detail. A programme is available for computing, from gamma-ray spectra, the detection limits of trace elements.<sup>109</sup>

Isenhour and Morrison<sup>110</sup> have developed a computer programme (based on an iterative process) which rapidly determines the optimum time of irradiation and decay for the activation analysis of any mixture. High-speed, computer-coupled, automatic systems for non-destructive medical and biological nuclear activation analysis have also been described.<sup>111</sup>

### *Mössbauer spectra*

Mössbauer spectra<sup>112</sup> which arise from the recoil-free nuclear resonant absorption of gamma-rays, are usually presented as plots of gamma-ray intensity as a function of the relative velocity between source and absorber. To separate the superimposed peaks in such a spectrum it is necessary to know the line shape. Theoretically it should be Lorentzian, but experimental effects can modify the shape to make it more Gaussian. With a digital computer it is possible to obtain the proper line shape and then generate a background response function, the theoretical and experimental curves being matched by a least-squares technique.

Duke and Gibb<sup>113</sup> have discussed in detail the application of computers to chemical calculations including, in particular, the numerical estimation of Mössbauer spectra parameters.

### MASS SPECTROMETRY

Computer techniques are now widely employed in high-resolution mass spectrometry, partly because the amount of information to be handled is excessively great for manual treatment and partly because conditions are particularly suited to the use of computers. Their main applications are the following.

- (i) Searching libraries of low resolution spectra of known compounds to permit identification of an unknown.
- (ii) Processing spectral data obtained both from electrical output and from photoplate instruments: the data may be fed directly, in digital form, to the computer or stored temporarily on magnetic tape.
- (iii) Presenting data in a clear and concise form.

- (iv) Deducing partial or complete structures.
- (v) Producing visual displays of data which may be edited by the operator before subsequent processing.
- (vi) Controlling spectral sweeps so as to obtain the necessary information from a spectrum.

In one example of a library search, a computer examined a store of 10000 spectra (in about 5 min) in an attempt to match the spectrum of an unknown. Any spectra that agreed sufficiently closely were drawn out on an X-Y recorder attached to the computer.<sup>114</sup> All the mass spectra were stored on magnetic tape as the mass value and intensity of each peak, together with the name and molecular weight of the compound.

#### *Elemental composition and data presentation*

Computer methods have been developed in which the atomic compositions of all the peaks in a high resolution mass spectrum are determined and presented in a relatively concise and intelligible way, thereby retaining much valuable information and saving much effort. The best known of these methods is the "element map" devised by Biemann, Bommer and Desiderio<sup>115</sup> and further described by McLafferty.<sup>116</sup> A good example is that of deoxydihydro-*N*-methylajmaline shown in ref. 117. This "element map" was constructed by an IBM 7094 computer in less than 30 sec, from line position and calibration data.<sup>117</sup>

Electrical recording can also be used to produce "element maps" when rapid scanning and high resolution are required.<sup>118,119</sup> The output signal is recorded on magnetic tape and stored, before being digitized and fed to the computer for processing. The possibility of processing data immediately they are obtained has also been discussed.<sup>119</sup> More recently, an automatic system for the preparation of such maps from high-resolution spectra recorded on photoplates has been described.<sup>120</sup> A special comparator-microdensitometer system reduced the time and manual effort while increasing the accuracy and resolving power.<sup>120,121</sup> The final stage in compiling an "element map" is the matching of each mass with a unique elemental formula, and several methods have been devised to accomplish this.<sup>122,123</sup>

Three other methods for data presentation in mass spectrometry have been described. The first of these involves the production of bar graphs, one for each set of ions with a given heteroatom content.<sup>124</sup> The second method uses a three dimensional figure in which the number of C atoms is represented by the major divisions of the *x*-axis, and the number of H atoms by the minor divisions, heteroatom content is plotted on the *y*-axis, and the relative abundances are represented by lines parallel to the *z*-axis.<sup>125</sup> Alternatively, the computer may be programmed to calculate and list the permitted combinations of atoms for which the ion masses agree within prescribed limits with the experimental values.<sup>126,127</sup>

#### *Structural interpretation*

The chief disadvantage of the methods above is that the information they convey loses clarity when large molecules with a high heteroatom content are involved. This has stimulated research into the use of computers to interpret spectra and to print out structures. Some success has been achieved in the analysis and sequencing of



small peptides,<sup>128-132</sup> which are particularly suited to this type of analysis. High-resolution data are compared with possible combinations of the exact masses of terminal groups and amino-acids, and the computed amino-acid sequence is printed out. Fragmentation of the amino-acids sometimes complicates the problem, but this can usually be detected. In one system, designed for cyclic as well as linear peptides, supplementary chemical evidence (such as qualitative or quantitative amino-acid analyses) can be accepted by the computer, checked against the molecular formula computed from the mass spectrum, and, if necessary, the formula can be corrected.<sup>131,133</sup>

A computer method has been described for determining the structures of saturated aliphatic hydrocarbons and carboxylic acids from C<sub>6</sub> to C<sub>30</sub>. When checked with methyl-substituted hydrocarbons, correct answers were obtained in about 78% of the runs, wrong answers in 2%, and about 20% were not calculated.<sup>134</sup>

Recognition of "ion types" by computer has been proposed as an extension to "element mapping,"<sup>135</sup> the "ion types" being classified according to the number of double bonds and rings, and the number and variety of heteroatoms present. A similar computer method has been described for searching for structural characteristics in the ions.<sup>136</sup>

The general problem of the use of computers to identify the functional groups in a molecule, from the mass spectrum, has been discussed.<sup>137</sup> Four empirical methods were mentioned, three involving derivation of "average" mass spectra and one using mass spectral correlations.<sup>137</sup> There is little doubt that as methods are developed, computer interpretation of mass spectra will be extended to larger molecules which fragment in less well defined ways.

#### *Other applications*

Advantages can result when the mass spectroscopist adds his experience and intuition to the speed and thoroughness of a computer, in solving a particular problem. In one case<sup>138,139</sup> fragmentation rules for the type of compound being examined were fed in, by typewriter, to a computer. In another,<sup>124</sup> data in computer storage were displayed on a cathode-ray tube so that the spectroscopist could decide on their rejection or retention.

Metastable transitions of ions in the mass spectrometer can assist in the interpretation of mass spectra and provide information about the nature of fragmentation. Automatic recording and processing have been described,<sup>140</sup> and the principle has been used to identify parent ions in peptide analysis.<sup>141</sup>

Mass spectrometry is particularly suited to accurate isotopic analysis, and several systems involving computer processing of such data have been described. These include the least-squares analysis and simplification of data for molecules containing elements with many isotopes,<sup>142</sup> and the electronic collection of data which are digitized and fed directly to a computer.<sup>143</sup> In two semi-automatic systems, data were collected for the isotopic analysis of solid samples.<sup>144</sup> A recorder-chart to punched-card converter and a computer programme allowed the determination of per cent abundance of each isotope and also the ratios of all isotopes to a preselected reference.<sup>145</sup>

Mass spectra of flash filament desorption products have been recorded repetitively and processed by a time-averaging computer to improve the signal-to-noise ratio.<sup>146</sup>

Gas chromatography is a very satisfactory technique to use in conjunction with a mass spectrometer and a computer, because fractions can be fed directly to the mass spectrometer for analysis and the data collected directly by the computer for storage and processing. This technique enables the analysis of submicrogram quantities of material. A system for fast-scanning, single-focussing mass spectrometers records data on magnetic tape for subsequent computer processing.<sup>147</sup> More recently,<sup>148</sup> a digital recording technique for low-resolution, fast-scanning mass spectrometers, employing a medium-sized on-line computer, has become available. Peak centre and intensity calculations proceed while the spectrum is being scanned, and the computer controls the scanning rate. Secondary storage on magnetic discs allows space for a large number of spectra. Results are printed as tables of mass *vs.* intensity, and as plots suitable for further processing (such as correcting for background or searching standard files of spectra). A similar system has been developed for fast-scan, high-resolution mass spectrometry.<sup>119</sup>

Methods of applying computers to process information obtained from a gas-liquid chromatograph-mass spectrometer system have also been considered.<sup>149</sup> Suitable techniques were described for use with the ASTM catalogue which lists the six strongest peaks in the mass spectra of 3200 substances.

Computer methods for the analysis of time-of-flight mass spectra have been discussed.<sup>150,151</sup> The practical problem of poor resolution can be partly overcome by calculating a "best" relative abundance for each ion in a sample, using least-squares methods. The characteristic pulse shapes are approximately Gaussian, and two methods for resolving the peaks in the presence of noise have been compared.<sup>150</sup>

#### CHROMATOGRAPHY AND AMINO-ACID ANALYSIS

Computer techniques have been applied in chromatography both in the treatment of data obtained from chromatographic separations and in theoretical calculations.

The output from analysis by gas chromatography, column chromatography with spectrophotometric measurement of eluted fractions,<sup>152</sup> or paper chromatography with suitable scanning to detect the solute spots<sup>153</sup> is commonly recorded as a series of peaks on a strip chart. The area under the peaks is required for the calculation of the composition of the sample being analysed. This may be estimated from height-width values, or measured with either a planimeter or an integrator with subsequent manual calculation of the analysis figures, but the use of a computer becomes desirable when large sets of data are involved. This problem is frequently encountered in automatic amino-acid analysis<sup>152</sup> and gas-chromatographic process control,<sup>154</sup> and in these applications computers can drastically reduce calculation time without loss of precision. The computer can also be programmed to control directly the process being monitored.<sup>154</sup>

For amino-acid analysis, programmes have been developed to accept manually punched data which may be either height-width measurements of the recorded peaks<sup>155,156</sup> or values of peak areas obtained from an integrator attached to the analyser.<sup>156</sup> Automatic card punching by the integrator is an improvement.<sup>156</sup>

A more sophisticated approach is the computer analysis of the transmission readings from the spectrophotometer, and methods have been described which enable such readings to be recorded directly on to punched cards, magnetic or paper

tape for computer analysis. The methods in general use require either an encoder attached to the shaft of the recorder balancing motor<sup>157-159</sup> or a digital voltmeter with punch facilities.<sup>160,161</sup> The computer is then programmed to monitor the data to determine the positions of peaks, edit the data to reduce noise, compensate for baseline variations, split unresolved peaks and calculate peak areas. The resolution of overlapping peaks has also been dealt with.<sup>48</sup> A programme has been described<sup>160</sup> which then requires the operator to select the peaks of interest before calculation of the analysis figures. This step can be eliminated by including in the input data the values of peak heights read from the recorder trace.<sup>162</sup> This identifies the peaks of interest in the order of their appearance, so that computing can be done in one step.

Where the amino-acid analysis is part of a protein composition determination, a programme is available which converts the results of the amino-acid analysis into the amino-acid composition of the protein, expressed as an integral residue number.<sup>163</sup>

These techniques are not limited to amino-acid analysis, and their application to general column chromatography has also been demonstrated.<sup>164</sup> In a similar manner, Bush<sup>153</sup> used a computer to analyse paper chromatogram data: this system is designed around a small laboratory computer rather than for the large computers in more general use.

The treatment of gas-chromatographic data by computer has been discussed,<sup>165-169</sup> and, as with amino-acid analysis, the computer usually applies corrections and calibration factors before calculating peak areas. One of these programmes has been adapted to calculate the results of semi-automatic CHN analysis.<sup>167</sup> Some of the systems described<sup>165,167,168</sup> use an analogue-to-digital converter for direct transmission of data to the computer. This idea can be extended, with one computer sampling in rapid succession the output of a group of chromatographs.<sup>165,170</sup> An alternative method is the integration analysis of the output of each chromatograph to determine peak areas, followed by computer calculation of composition figures.<sup>170</sup>

Various aspects of chromatographic theory have been investigated by authors who have used computers for the necessary calculations. Few programmes have been published in detail, but available descriptions suggest that most of them are limited in application and that most authors develop their own programmes to suit their particular needs. Examples include the prediction of the shapes and positions of elution curves,<sup>171</sup> the calculation of parameters in programmed-temperature gas chromatography,<sup>172</sup> the determination of adsorption rate constants from the change in shape of a pulse of adsorbate as it is transported through a packed column,<sup>173</sup> a theoretical-plate treatment of partition chromatography,<sup>174</sup> an analysis of the behaviour of wide feed-bands in a chromatographic column,<sup>175</sup> the simulation of the operation of a chromatography column,<sup>176</sup> the determination of the optimum analysis conditions for the separation by gas chromatography of a complex mixture,<sup>177</sup> and the selection of the best ratio of binary or ternary liquid packings for gas chromatography.<sup>178</sup> A programme has been written to assist a study of isotope fractionation during chromatography of doubly labelled compounds.<sup>179</sup> This programme permits the mathematical synthesis and combination of Gaussian peaks and has also been applied in a study of the effects of impurities on displacement and band broadening of chromatographic peaks<sup>180</sup> and in the detection and analysis of up to four components in an unresolved multiplet.<sup>181</sup>

## ELECTROANALYTICAL CHEMISTRY

Three papers in a recent symposium on electroanalytical chemistry were concerned with systems for the automatic collection of electroanalytical data in a digital form suitable for computer processing.<sup>182-184</sup> Such systems overcome the need to photograph and measure oscilloscopic traces and to apply corrections to the data: some flexibility in technique may be obtained by the use of a patchboard control.<sup>184</sup>

Breiter<sup>185</sup> has described a method for the automatic digital collection of voltammetric data on paper tape, as well as the main features of three programmes for subsequent computer processing of the data. The method and programmes have been extended to galvanostatic and potentiostatic data.<sup>186</sup>

Because most electroanalytical techniques have much in common, a flexible system capable of being employed at any one time in one of several techniques is feasible and economic. A system has been devised in which a small digital computer is programmed to initiate an experiment, to acquire and store the data in digital form, to test for the completion of a run, and to perform functional analysis, such as least-squares fitting, on the stored data.<sup>187,188</sup> It was tested with some chronocoulometric experiments,<sup>187</sup> and examples were given of other possible applications.<sup>188</sup>

In an experimental procedure for fast-sweep polarography,<sup>189</sup> a small digital computer was used on-line for the resolution of closely spaced reduction waves and for "ensemble-averaging" which extended the analytical sensitivity by at least an order of magnitude.<sup>189</sup> The effects of background noise on the computer processing were investigated, and practical examples of the use of the system were outlined.

A programme, POLARGRM, computes the least-squares straight line, the slope and the half-wave potential, together with the standard deviations of the last two, for the conventional semi-log (Heyrovský-Ilkovič) plot of current-potential data from experimental polarograms.<sup>190</sup> Successive formation constants for the cadmium-thiocyanate system have been calculated from polarographic data, using a computer.<sup>191</sup>

The technique of cyclic chronopotentiometry, in which the applied current is reversed at each transition, has been described.<sup>192</sup> Equations for the successive transition times for linear diffusion in a single component system were derived and solved by an iterative method on a digital computer; the necessary programme is given.

Other instances in which computers have been used in processing electrochemical data include the calculation of rate constants of adsorption reactions from voltammetric current-potential curves or galvanostatic potential-time curves,<sup>193</sup> and a mathematical analysis of the potential-sweep method for a charge-transfer reaction of the type  $A^- \rightarrow A + e_0^-$ .<sup>194</sup>

## LIQUID-LIQUID EXTRACTION

In many cases, liquid-liquid extraction provides a simple and convenient method for separating an element required for analysis from other interfering elements. It is desirable to be able to predict the experimental conditions required to produce an effective separation. Although computers provide a ready means for performing the calculations, efforts in this direction have met with mixed success, probably because, at present, the theory is largely empirical.

Measured distribution coefficients can be used to calculate the number of stages required to effect a good separation. Berg and Sanders<sup>195</sup> have developed two short

programmes to calculate the separation in a 100-stage countercurrent extractor based on the design of Craig and Post.<sup>196</sup> They studied the distribution of bromo-complexes of the platinum group metals between hydrobromic acid and several solvents. Agreement between experiment and calculation was poor. A facility for altering the ligand concentration at several points in such an extractor was incorporated, and a programme was developed for calculating the distribution of solute.<sup>197</sup> Experimental studies on the extraction of a number of elements, using isobutyl methyl ketone as solvent and hydrochloric acid as ligand, gave results which agreed satisfactorily with predictions.<sup>197</sup>

Counter double current distribution has been simulated on a digital computer. General equations were derived which were claimed to describe adequately the previously reported analytical data for the separation of fatty acids.<sup>198</sup> The effects of varying the number of stages has also been examined.<sup>199</sup> A countercurrent multi-stage extraction system has been simulated on an analogue computer.<sup>200</sup>

#### INFORMATION RETRIEVAL

A development with far-reaching implications is the retrieval of chemical information by computer. The information-handling and publication operations of the Chemical Abstracts Service are being converted steadily into computer-based procedures which prepare a wide range of printed and machine-readable services from supplied data. Examples of the former are the current-awareness journals "Chemical-Biological Activities", "Chemical Titles" and "Polymer Science and Technology," based on the use of a KWIC<sup>201</sup> (Key Word in Context) programme. "Basic Journal Abstracts" and "CA Condensates" are examples of services available on computer tapes. Related examples are the MEDLARS service (provided by the United States National Library of Medicine, Bethesda) and the Science Citation Index and the Automatic Science Citation Alert (of the Institute for Science Information). This field, which has recently been reviewed,<sup>202</sup> is at present expanding rapidly.

Complete descriptions of the topology of chemical molecules can be stored and manipulated by computer. For example, the Chemical Compound Registry of the Chemical Abstracts Service stores the structures of over 700,000 compounds.<sup>203</sup> Machine-searching of such computer files can greatly facilitate the location of single compounds or of all compounds possessing certain structural features in common. Several ways of storing and retrieving such information have been described.<sup>204</sup>

Storing and searching numerical data have also been mentioned elsewhere in this review.

**Zusammenfassung**—Digitalrechner finden jetzt bei einer großen Anzahl chemischer Probleme Anwendung. Für analytische Chemiker besonders interessante Gebiete wie statistische Datenverarbeitung, Röntgenanalyse, Spektroskopie, Massenspektrometrie, Gaschromatographie und elektroanalytische Chemie werden diskutiert.

**Résumé**—Des ordinateurs analogiques sont couramment appliqués à un large domaine de problèmes chimiques. On discute d'aspects d'intérêt particulier pour les chimistes analystes, comprenant le traitement statistique, l'analyse aux rayons X, la spectroscopie, la spectrométrie de masse, la chromatographie en phase gazeuse et la chimie électroanalytique.

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## PRECIPITATION FROM HOMOGENEOUS SOLUTION OF CATIONS RELEASED FROM EDTA COMPLEXES

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**Summary**—The suitability of EDTA complexes for use in precipitation of certain cations from homogeneous solution under various experimental conditions can be predicted from a knowledge of the solubility product of the compound to be precipitated and the complex stability constant. A brief review of previous work in the field of masking effectiveness is given. An examination of factors influencing precipitation has been carried out. It is shown that a simple ratio can be used for predicting the likelihood of precipitation at various pH values and that more rigorous theoretical approaches are not necessarily more advantageous.

PRECIPITATION from homogeneous solution by cation release at constant pH may be effected by first complexing the cation with EDTA and then releasing it into a solution containing the precipitating agent, at a controlled rate by oxidative destruction of the EDTA.<sup>1</sup> The masking efficiency of complexing agents has been considered by Cheng<sup>2</sup> and Tanaka,<sup>3</sup> and a different approach by Hulanicki<sup>4</sup> has been extended by Kelly and Sutton,<sup>5</sup> who give a brief review of the results of the previous workers. Although it is important to know the concentration of the metal left in solution, it is essential for precipitation from homogeneous solution that no reaction should occur on first addition of the precipitating anion. This is especially true when the oxidative method is employed, since all the masking agent is eventually removed from the solution. Although the possibility of the precipitation occurring can be determined experimentally it would be of great advantage if it could be easily predicted from a simple knowledge of the stability constant of the complex and the solubility product of the precipitated salt. In the following treatment it is shown that a simple ratio relating these quantities can be used and that a more rigorous approach, in which all the factors considered by the previous workers are included, is not necessarily more advantageous.

For a metal complexed with ligand Y and to be precipitated as the salt  $M_jA_i$ , Kelly and Sutton's final equation relating the concentration of the metal ion remaining in solution to the most important experimental factors took the form:

$$pM' = \frac{1}{j} (pS + i \log[A]) - i/j \log \alpha_{A(H)} - \log \alpha_{M(Y)} \quad (1)$$

where

$pM'$  = negative logarithm of the concentration of metal predicted to remain in solution

$pS$  = negative logarithm of the solubility product of  $M_jA_i$

$[A]$  = analytical concentration of the precipitating anion

$[Y]$  = analytical concentration of the complexing ligand

$K_{MY}$  = stability constant of the complex

TABLE I.—TO DEMONSTRATE THE INFLUENCE OF EXCESS OF REAGENT ON THE VALUE OF  $pM'$  AS DETERMINED BY EQUATION (1)

Precipitation of lead as sulphide from lead-EDTA complex at pH 3.2										
Excess of precipitating anion, %	0	10	100	200	10	100	200	0	0	0
Excess of complexing agent, %	0	10	100	200	0	0	0	10	100	200
$pM'$	7.60	7.60	7.60	7.60	7.64	7.90	8.08	7.56	7.30	7.12
Difference in $pM'$ from conditions with no excess, %		0	0	0	+0.5	+5.0	+6.3	-0.5	-4.0	-6.3
Precipitation of silver as sulphide from silver-EDTA complex at pH 10.0										
Excess of precipitating anion, %	0	10	100	200	0	0	0	10	100	200
Excess of complexing agent, %	0	10	100	200	10	100	18.03	17.84	17.58	17.40
$pM'$	17.9	17.76	17.72	17.64	17.9	18.03	18.12	17.84	17.58	17.40
Difference in $pM'$ from conditions with no excess, %		-0.8	-1.3	-1.5	0	+0.8	+1.5	-0.2	-1.5	-2.8
Precipitation of silver as phosphate from silver-EDTA complex at pH 11.3										
Excess of precipitating anion, %	0	10	100	200	0	0	0	10	100	200
Excess of complexing agent, %	0	10	100	200	10	100	200	0	0	0
$pM'$	-1.55	-1.57	-1.75	-1.87	-1.57	-1.49	-1.43	-1.57	-1.83	-2.01
Difference in $pM'$ from conditions with no excess, %		+1.2	+13.0	+20.5	-1.0	+4.0	+7.7	-1.3	-18.0	-29.5

$\log \alpha_{A(H)}$  and  $\log \alpha_{Y(H)}$  are the side-reaction coefficients<sup>6</sup> describing the masking of the precipitating anion and the complexing anion by hydrogen ions respectively, and  $\alpha_{M(Y)} = 1 + K_{MY}[Y]/\alpha_{Y(H)}$ .

The authors claim that the error involved on application of the equation is one unit in the  $pM'$  value, and the average error for the empirical determination of the extent of precipitation is less than 10%. Since the equation is derived on the assumption that the complexing and precipitating agents are in excess, it was considered of interest to find how variation in concentration of these reagents would affect the  $pM'$  value. Examples of calculations for a number of salts of variable stoichiometry are given in Table I, from which a number of conclusions may be drawn.

The effect is very dependent on the stoichiometry of the precipitated salt, and for low  $pM'$  values the effect can be excessively and misleadingly large.

The main factors contributing to an error in  $pM'$  as calculated from equation (1) are (a) the variation in the reported values of solubility products and stability constants,<sup>7</sup> (b) the influence of ionic strength (the experimental conditions of analysis are often greatly different from those for determination of stability constants *etc.*), (c) hydrolysis, *e.g.*, the formation of hydroxo-complexes of the type  $M(OH)_n$ -EDTA at higher pH values,<sup>8</sup> which may alter the value of the apparent stability constant when this is calculated only from a consideration of the masking of the complexing ligand by hydrogen ions,<sup>9</sup> and (d) the effect of temperature.<sup>10</sup>

It can be argued that the uncertainty in the accuracy of equation (1) would justify a simpler equation, especially when the complex is decomposed by destruction of the ligand.

#### The $pM_s/pM_c$ ratio

The two main factors in the formation of a precipitate by cation release from complexes are the concentration of metal ion,  $M_c$ , resulting from the dissociation of the complex, and the concentration of metal ion,  $M_s$ , calculated from the solubility product of the insoluble salt. Ideally, when  $pM_s/pM_c = 1$  an equilibrium is reached at which the ion is on the verge of precipitation. If the ratio is  $>1$  precipitation will occur, whereas the ion will remain in solution for ratios  $<1$ .

Under experimental conditions when the precipitating agent A is in excess,<sup>5</sup>

$$pM_s = \frac{1}{j} (pS + i \log[A']) \quad (2)$$

where  $[A']$  is the concentration of free precipitating anion. If the side-reaction is taken into account<sup>4</sup>

$$\alpha_{A(H)} = [A]/[A']$$

where  $[A]$  is the analytical concentration of precipitating anion and  $\alpha_{A(H)}$  is the side-reaction coefficient, it follows that

$$pM_s = \frac{1}{j} pS + i/j \log[A] - i/j \log \alpha_{A(H)} \quad (3)$$

The  $pM_c$  value can be derived from the stability constant  $K_{MY} = [MY]/M_c[Y']$  where  $[MY]$ ,  $M_c$  and  $[Y']$  are the concentrations of the complex, the free hydrated cation and the ligand free for complexation.

For a strong complex  $[MY] \gg M_c$  and therefore  $[MY] \sim [M]$ , the analytical concentration of metal ion. It can be shown that this assumption is essentially true when the conditional stability constant of the complex is  $>10^4$ . The free ligand concentration can be expressed<sup>4</sup> as  $\log[Y'] = \log[Y] - \log \alpha_{Y(H)}$ .

Thus the ratio  $pM_s/pM_c$  becomes

$$\frac{pM_s}{pM_c} = \frac{1/j pS + i/j \log[A] - i/j \log \alpha_{A(H)}}{\log K_{MY} + \log[Y] - \log \alpha_{Y(H)} - \log[MY]} \quad (4)$$

In this equation  $[MY]$  is not known accurately since the concentration of the metal ion

TABLE II.—COMPARISON OF VALUES OF  $pM_s$  AND  $pM_c$  FROM THE COMPLEX AND SIMPLIFIED EQUATIONS

Compound	pH	Equation (4)			Equation (5)			Result
		$pM_s$	$pM_c$	$pM_s/pM_c$	$pM_s$	$pM_c$	$pM_s/pM_c$	
Bi <sub>2</sub> S <sub>3</sub>	1.4	21.00	14.30	1.47	19.33	7.10	2.72	Precipitation
Bi <sub>2</sub> S <sub>3</sub>	10.0	42.00	28.60	1.47	19.33	14.80	1.31	
AgCl	10.3	8.77	8.40	1.15	4.89	4.60	1.06	
Ag <sub>2</sub> S	10.0	22.40	8.10	2.77	16.20	4.55	3.56	
PbS	3.2	14.20	8.90	1.60	14.50	4.85	2.99	
PbS	10.0	25.00	18.80	1.34	14.50	9.90	1.46	
PbCrO <sub>4</sub>	2.5	n.d.	8.30	n.d.	6.88	4.00	1.72	
CaF <sub>2</sub>	3.8	7.81	3.00	2.60	3.67	2.00	1.84	
BaCrO <sub>4</sub>	4.3	n.d.	1.50	n.d.	4.85	1.15	4.22	
BaSO <sub>4</sub>	4.5	9.01	1.70	5.30	5.00	1.35	3.70	
BaSO <sub>4</sub>	7.6	9.01	6.40	1.41	5.00	3.65	1.37	
ZnS	10.0	19.00	17.50	1.09	11.50	9.25	1.24	
Ag <sub>2</sub> SO <sub>4</sub>	9.5	1.96	7.80	0.25	1.54	4.35	0.35	
Ag <sub>3</sub> PO <sub>4</sub>	11.3	5.31	8.60	0.62	4.32	4.70	0.92	
Ag <sub>2</sub> CrO <sub>4</sub>	10.0	5.48	8.10	0.68	3.89	4.55	0.86	
PbCl <sub>2</sub>	3.6	2.77	9.50	0.29	1.79	5.30	0.34	
PbF <sub>2</sub>	3.5	4.83	9.50	0.51	2.67	5.30	0.50	
PbSO <sub>4</sub>	3.8	6.74	10.30	0.64	3.88	5.65	0.69	
CaSO <sub>4</sub>	3.6	3.62	2.20	1.65	2.31	1.65	1.40	
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	6.4	3.56	8.00	0.45	4.93	4.50	1.09	
Fe(OH) <sub>3</sub>	6.5	13.40	22.40	0.60	9.74	11.70	0.83	
FePO <sub>4</sub>	5.5	7.00	20.90	0.34	8.20	10.95	0.75	
BaF <sub>2</sub>	4.6	3.77	1.70	2.22	2.12	1.35	1.57	
MnS	9.1	10.20	13.90	0.73	7.60	7.42	1.02	

n.d. = not determined.

is the analytical problem. However, the concentration of metal is usually known approximately, and if not, can be estimated by complexometric titration during the addition of the excess of ligand. Such an estimate would not be more inaccurate than the values of  $K_{MY}$  and  $\log \alpha_{Y(H)}$ .

The  $pM_s/pM_c$  ratios for a number of compounds, assuming 0.1M complexing ligand and precipitating anion at different levels of pH, are shown in Table II.

#### Simplified derivation of $pM_s/pM_c$ ratio

The derivation of equation (4) is based on the assumption that the complexing and precipitating agents are in great excess, e.g., 0.1M. This is not necessarily the case<sup>11</sup> and often only a very small excess of either reagent is used. Then, for an

insoluble compound  $M_jA_i$  with solubility product  $S = [M]^j[A]^i$ ,  $pM_s = (pS - i \log j/i)/(i + j)$ . The stability constant for the complex  $MY$  is  $K_{MY} = [MY]/M_c[Y]$  and if it is assumed that  $M_c \sim [Y]$ , then

$$pM_c = \frac{1}{2}(\log K_{MY} - \log[MY])$$

The effect of the pH of the solution may be allowed for by the use of the apparent constant<sup>9</sup>  $\log K_{MY}'$  calculated from reported values of stability constants. The expression for the  $pM_s/pM_c$  ratio, under the conditions of a small excess of complexing and precipitating agents, becomes

$$pM_s/pM_c = \frac{\frac{1}{j+i}(pS - i \log j/i)}{\frac{1}{2}(\log K_{MY}' - \log[MY])} \quad (5)$$

As in the case of the extensive treatment the approximate concentration of the metal ion must be known.

This derivation of  $pM_c$  has been used by Cartwright,<sup>12</sup> who assumed, however, that  $[MY]$  was  $1M$  and hence  $\log[MY]$  was zero. Cheng<sup>2</sup> made a similar assumption in calculation of his quantity  $pM_m$ . This assumption can lead to appreciable errors, particularly when the value of  $\log K_{MY}$  is small.

Calculated values from equation (5) are found in Table II.

## CONCLUSIONS

Table II shows that in a number of cases there is a significant difference between the values for  $pM_s/pM_c$  calculated with the extended equation (4) and the simple one (5). The main discrepancy is for bismuth sulphide at pH 1.4 where  $pM_s$  values differ considerably in relation to the  $pM_c$  values. This is because of the effect of a very large value of  $\log \alpha_{A(H)}$  representing a high degree of masking of the sulphide ion at low pH values.

Otherwise, when the results of the two different approaches are compared, the end products differ only slightly. Precipitation does occur for values of  $pM_s/pM_c > 1$  except for barium fluoride and calcium sulphate for which the explanation lies probably in the uncertainty of calculated values for  $pM_c$  ( $\log K_{MY} < 4$ ) and the relatively high solubility of the compounds.

If a graph is plotted of  $pM_s$  vs.  $pM_c$ , a line drawn between compounds which are precipitated and those which are not has a slope very near to unity. The equation (4), which is theoretically more accurate, gives rise to a line passing through the origin, but equation (5) gives a wider range of uncertainty contained between two parallel lines cutting the abscissa within the limits of  $pM_c$  of 0 and  $-1$ . One can conclude that bearing in mind the approximations made, the final result obtained with the simple approach is quite satisfactory.

### *Introduction of the pH term into equation (5)*

Since the masking efficiency of the complexing agent depends on the hydrogen ion concentration it might be useful to have an equation available in which the pH term is involved. This would allow a rapid calculation of the approximate pH at which precipitation would be prevented on the initial addition of the precipitating agent.

The apparent or conditional stability constant of the metal-EDTA complex is represented by<sup>9</sup>

$$\log K_{MY}' = \log K_{MY} - \log \alpha_{Y(H)} \quad (6)$$

The relationship between  $\log \alpha$  and pH is well known,<sup>9</sup> and a plot of  $\log \alpha$  against  $\log pH$  over a range of pH 1.7–12.0 gives a straight line represented by the equation

$$\log pH = 1.02 - (\log \alpha)/20 \quad (7)$$

Using relationship (6) and approximating the value 1.02 to 1.0 the last equation can be rearranged as

$$\log K_{MY}' = 20(\log pH - 1) + \log K_{MY} \quad (8)$$

On substitution for  $\log K_{MY}'$  in the expression for  $pM_c$ , equation (5) takes the form

$$pM_s/pM_c = \frac{2}{(j+i)} \left\{ \frac{pS - i \log j/i}{20(\log pH - 1) + \log K_{MY} - \log [MY]} \right\} \quad (9)$$

The pH value at which the precipitation of the metal ion will be prevented can be calculated, at least approximately, from this final equation.

Since many complexing agents do not give a smooth curve for a plot of pH *vs.*  $\log \alpha$ , the application of equations such as (7) is limited. However, the approach can be applied to a number of complexing agents, e.g., for 1,2-diaminocyclohexanetetraacetic acid (DCTA) the relationship is approximately

$$\log pH = 1.1 - (\log \alpha)/21$$

over a pH range 2–12.

## EXPERIMENTAL

### Reagents

EDTA, 0.05M. All other reagents were of analytical grade and 0.1M stock solutions were prepared.

### Apparatus

To avoid providing sites for nucleation, all experiments were carried out in clean unscratched beakers; pH measurements were made to  $\pm 0.05$  with a pH meter.

### Method

A number of cations were examined to see whether under the conditions of the experiments they would remain in solution or be precipitated spontaneously from their complexed form by a range of anions. The metals studied were selected to cover a wide range of stability constants.<sup>7</sup>

Five ml of stock solution of the metal ion to be precipitated were treated with 10.25 ml of EDTA solution (representing a 2.5% excess)\* in a 250-ml beaker, then diluted with 80 ml of distilled water. The pH was then adjusted by addition of nitric acid or sodium hydroxide, or in some cases with buffer solution, e.g., when sodium sulphide or trisodium phosphate was used to provide the precipitating anion. The precipitating anion was then introduced by addition of 5 ml of a stock solution of the appropriate sodium salt. A summary of the compounds precipitated and the pH of the solution at which the experiment was carried out are given in Table II.

**Zusammenfassung**—Die Eignung von EDTA-Komplexen zur Fällung bestimmter Kationen aus homogener Lösung unter verschiedenen Bedingungen kann bei Kenntnis des Löslichkeitsproduktes des zu fällenden Niederschlages und der Stabilitätskonstanten des Komplexes

\* Shown from calculations based on Kelly and Sutton's equation to be negligible (see Table I).

vorausgesagt werden. Es wird ein kurzer Überblick über die Maskierungswirksamkeit gegeben. Die Faktoren, die die Fällung beeinflussen, wurden untersucht. Es wird gezeigt, daß man ein einfaches Verhältnis zur Vorhersage der Wahrscheinlichkeit einer Fällung bei verschiedenen pH-Werten verwenden kann; theoretisch strengere Lösungswege des Problems bringen nicht unbedingt mehr Vorteile.

**Résumé**—On peut prévoir la valeur de complexes d'EDTA pour l'emploi dans la précipitation de certains cations à partir de solutions homogènes dans diverses conditions expérimentales à partir d'une connaissance du produit de solubilité du composé à précipiter et de la constante de stabilité du complexe. On présente une brève revue des travaux antérieurs dans le domaine de l'efficacité de dissimulation. On a procédé à un examen de facteurs influençant la précipitation. On montre qu'on peut utiliser un rapport simple pour prévoir la probabilité de précipitation à diverses valeurs du pH et que des approches théoriques plus rigoureuses ne sont pas nécessairement plus avantageuses.

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## GRUNDLAGEN DER GRADIENT-DÜNNSCHICHT- CHROMATOGRAPHIE AUF "SAUER-BASISCHEN" KIESELGEL-SCHICHTEN

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**Zusammenfassung**—Einleitend sind die Möglichkeiten und bisherigen Anwendungen der Gradient-Dünnschicht-Chromatographie kurz zusammengestellt. Die Ergebnisse dieser Technik, insbesondere der pH-Gradient-DC, waren vor Beginn dieser Arbeit noch nicht gut reproduzierbar; vor allem waren die Schichten in Bezug auf den Verlauf des pH-Gradients nicht gekennzeichnet. In der vorliegenden Arbeit werden nun Vorschriften für die reproduzierbare Herstellung fehlerfreier pH-Gradient-Schichten gegeben. Diese Schichten lassen sich durch die Angabe des pH-Wertes als Funktion des Ortes charakterisieren. Damit sind erstmals pH-Gradient-Schichten mit definierter Gradient-Ausbildung gegeben. Abschließend sind die bei der pH-Travers-Gradient-Chromatographie auf solchen Schichten erhaltenen typischen Kurvenformen einzelner Substanzklassen zusammengestellt und kurz erläutert.

SEIT 1958 ist die Dünnschicht-Chromatographie (DC) in ihrer heutigen Form bekannt<sup>1</sup> und hat als Trennmethode für Mikro- und Nanogramm-Mengen weltweite Verbreitung erfahren.<sup>2-6</sup> Meist wird dabei so verfahren, daß man versucht, ein gegebenes Trennproblem auf einer uniformen Sorptionsschicht durch Wahl eines geeigneten Fließmittels zu lösen. Man nahm also seit den Anfängen der DC Änderungen bezüglich der mobilen Phase vor. Einer Variation in den Eigenschaften der stationären Phase—dabei ist an eine Teilimprägnierung eines Sorptionsmittels bzw. an die Aufgabe zweier oder mehrerer Sorptionsmittel auf dieselbe Trägerglasplatte gedacht—kam lange Zeit keine Bedeutung zu. Diese Entwicklung ist zweifellos darauf zurückzuführen, daß die uniformen Schichten zumeist den bisherigen Anforderungen genügten und ferner die Zusammensetzung des Fließmittels leichter zu verändern ist als die Schichteigenschaft.

Grundsätzlich sind zwei Änderungen bzgl. der Schichteigenschaften denkbar, nämlich

—diskontinuierliche, stufenartige und

—kontinuierliche, stetige Übergänge von einer Eigenschaft zu einer anderen in der Schicht.

Solche stufenlose Übergänge in den Eigenschaften der stationären Phase in der Dünnschicht- und Säulen-Chromatographie wurden durch die Einführung der Gradient-Technik von Stahl<sup>7-9</sup> ermöglicht. Unter einem Gradient versteht man die kontinuierliche Änderung einer Eigenschaft bzw. den gleitenden Übergang von einer

Eigenschaft zu einer anderen. Für die DC sind folgende Fälle<sup>8</sup> denkbar:

- Übergang von einem Sorbens zu einem anderen, z.B. von Kieselgel zu Cellulose.
- Gradient in der Imprägnierung, z.B. von 0–5% Silbernitrat
- pH-Gradient, z.B. sauer-basisch
- Korngrößengradient, z.B. feinkörnig-grobkörnig
- Schichtdickengradient

Auf einer solchen Gradientschicht stehen im Gegensatz zu uniformen Schichten drei verschiedene Laufflächen zur Verfügung.<sup>7</sup> Dies soll an einem Gradient "aktiv-inaktiv" z.B. Kieselgel-Kieselgur erläutert werden (vgl. Abb. 9 in Ref. 7 oder Abb. 2 in Ref. 8 und 9). Es kann nämlich mit oder *im* Gradient von "aktiv" in Richtung "inaktiv" chromatographiert werden sowie auch in der entgegengesetzten Richtung. Diese Technik eröffnet die Möglichkeit, den Abstand zwischen nahe beieinanderliegenden Zonen zu vergrößern, bzw. bei weit auseinanderliegenden Zonen zu verringern, was besonders bei quantitativen oder mikropräparativen Arbeiten vorteilhaft ist.<sup>9</sup> Außerdem kann *quer* zum Gradient-Verlauf chromatographiert werden. Für diese zweifellos interessanteste Anwendungsform wurde die Bezeichnung Travers-Gradient-Technik (T-Gradient) vorgeschlagen.<sup>8,9</sup>

Zur Demonstration der Leistungsfähigkeit dieser neuen Technik wurde in der ersten Mitteilung<sup>7</sup> über das chromatographische Verhalten von Fettfarbstoffen in einem Sorbens-T-Gradient Kieselgel-Kieselgur sowie über das Verhalten von Indikatorfarbstoffen und Alkaloiden in einem pH-Gradient berichtet.

An der gleichen Stelle wird auch ein Gerät zur Herstellung von Gradient-Schichten beschrieben und die Arbeitsvorschrift dazu gegeben. Dieser sog. GM-Streicher (Fa. Desaga) (G = Gradient, M = Mischer) läßt sich mit einigen Zusatzteilen aus dem zur Herstellung von uniformen Schichten benutzten Grundgerät zusammenstellen.

In den Jahren 1964–66 wurde von dieser Technik in unserem Arbeitskreis zur Trennung von weiteren Substanzklassen Gebrauch gemacht: Nach der Ermittlung einer optimalen Konzentration der Silbernitrat-Imprägnierung gelang Vollmann<sup>10,11</sup> die Auftrennung eines Gemisches von Terpenalkoholen und Pfeifle<sup>12,13</sup> die Auftrennung der Pyrethringruppe aus Pyrethrum-Extrakten, wobei sechs einander sehr ähnliche Verbindungen identifiziert werden konnten. Die pH-T-Gradient-Chromatographie setzten Stahl<sup>8</sup> bei Ipecacuanha-Alkaloiden und Schorn<sup>14</sup> bei hydrophilen Stoffgemischen mit Erfolg ein. Desgleichen berichten Stahl<sup>8,9</sup> bei Aminosäuren sowie auch Schorn<sup>14</sup> von den Vorteilen eines Sorbens-T-Gradients. Rozumek<sup>15</sup> setzt die Chromatographie im Silbernitrat-Gradient bei der Trennung der Hauptalkaloide und -sapogenine von *Solanum dulcamara* ein. Außerhalb dieses Arbeitskreises bedienten sich Shellard *et al.*<sup>16</sup> bei Untersuchungen über Mitragyna-Alkaloide, Polderman<sup>17</sup> bei der Stabilitätsprüfung von Hormonen sowie auch Haeussler<sup>18</sup> der neuen Technik, die neuerdings auch auf Ionenaustauscherschichten angewandt wurde.<sup>19</sup>

Ziel der vorliegenden Arbeit war es, Vorschriften für die Herstellung von pH-Gradient-Schichten mit verschiedenen pH-Intervallen zu ermitteln und die einzelnen Schichten bzgl. ihres Gradient-Verlaufs zu charakterisieren. Darauf fußend sollte dann das chromatographische Verhalten typischer pH-abhängiger Substanzklassen untersucht werden.

## HERSTELLUNG VON KIESELGEL-SCHICHTEN MIT EINEM DEFINIERTEN pH-GRADIENT

### *Allgemeingültige Bedingungen für die Herstellung von pH-Gradient-Schichten*

Soll der Neutralpunkt ungefähr in der Schichtmitte liegen, so muß, wenn man einmal vom Einfluß des Sorptionsmittels selbst absieht, mit etwa gleichen Volumina von Lösungen der gleichen Konzentration an Säure, bzw. Base gearbeitet werden.

Es sollte überprüft werden, ob die damit bereiteten Suspensionen auch etwa gleiche Volumina haben, damit beim Herausheben der Diagonaltrennwand des GM-Streichers sich nicht eine Suspension über die andere schiebt.

Weiterhin ist es erforderlich, daß die Einzelsuspensionen annähernd gleiche Viskositäten besitzen, damit aus den zum Anschütteln (bzw. Anreiben) benutzten Gefäßen etwa gleiche Mengen in die beiden Teilerräume des GM-Streichers gelangen. Etwa gleiche Viskositäten sind auch Voraussetzung für eine gute Durchmischung der Suspensionen und zur Erzielung gleicher Schichtdicken beim Ausstreichvorgang.

Nach unseren Erfahrungen muß zur Erzielung der gleichen pH-Skala auf allen Platten die Suspensionsmenge so bemessen sein, daß nach dem Ausstreichen noch ein Rest im Streicher vorhanden ist. Die Mischerhülse soll dabei nicht ganz bis zum oberen Rand der Kreisscheiben sondern nur zu etwa  $4/5$  der Kreisscheibenhöhe gefüllt werden. Von entscheidender Bedeutung ist nun, daß sich die durch die Vermischung der Einzelsuspensionen entstehende Gesamtsuspension überhaupt austreichen läßt (vgl. S. 5 u. 6).

Nach dem Ausstreichen sollen die Schichten schnell und möglichst gleichmäßig austrocknen, und zwar alle fünf Schichten sowie alle Bereiche jeder einzelnen Schicht gleichzeitig.

### *Auswahl von Säure und Base*

Es interessierten in erster Linie pH-Gradient-Schichten mit einem möglichst großen pH-Intervall, da das Chromatographieren auf einer solchen Schicht einen Überblick über das Trennverhalten bei allen im Intervall eingeschlossenen pH-Werten gibt. Dabei können dann evtl. die für einen speziellen Fall geeigneten Bedingungen erkannt und Schichten mit einem entsprechenden, kleineren pH-Bereich bereitet werden. Zur Herstellung kamen also nur die sehr starken Säuren und Basen infrage. In der Kieselgel-Schicht findet eine Neutralisation der Säure mit der Base statt. Um nun eine möglichst einfache Ausbildung des Gradienten mit nur einem Äquivalenzpunkt zu erzielen, wurde darauf geachtet, nur einwertige Säuren und Basen zu verwenden. Weiterhin war es Voraussetzung, daß die zur Imprägnierung des Kieselgels verwandten Säuren und Basen bei der Herstellung und Vorbereitung der Schichten zur Chromatographie erhalten blieben, d.h. speziell, daß sie sich beim Aktivieren des Kieselgels bei  $110-120^\circ$  nicht verflüchtigten. Für alle folgenden Versuche wurden Schwefelsäure, bzw. Natronlauge verwandt.

### *Versuche mit Kieselgel H*

Zunächst wurden Versuche zur Ermittlung der zu erwartenden pH-Grenzwerte der Gradient-Schichten durchgeführt. Dazu wurde Kieselgel H (Fa. Merck) benutzt, das auch zur späteren Herstellung der pH-Gradient-Schichten dienen sollte, da man dabei gegenüber dem schnell "austrocknenden" Kieselgel G (Fa. Merck) mehr Zeit zur experimentellen Ermittlung geeigneter Arbeitsvorschriften zur Verfügung hat.

### Ermittlung der pH-Intervallgrenzen

Die Diagonaltrennwand des GM-Streichers endet im Abstand von je 15 mm von den Schmalseiten des Teilertrags. Es kann näherungsweise angenommen werden, daß in den Räumen zwischen den Enden der Trennwand und den längsseitigen Trogwänden die beiden Suspensionen unvermischt bleiben, d.h. auf der einen Seite bleibt ein Anteil der sauren und auf der anderen Seite der basischen Suspension erhalten. Es mußte daher mit uniform sauren, bzw. alkalischen Schichten möglich sein, die auf Gradient-Schichten zu erwartenden pH-Grenzwerte zu ermitteln. Gleichzeitig konnten dabei Erfahrungen über das Verhalten von Kieselgel gegenüber Säuren und Basen gesammelt werden, z.B. mit welchen Ausgangskonzentrationen man zur Chromatographie brauchbare uniforme saure, bzw. basische Schichten herstellen kann.

*Uniform alkalische Schichten.* Unter Verwendung von Kieselgel H wurden mit Natriumhydroxid-Lösungen im Konzentrationsbereich von 0,5*N* bis 2*N* alkalische Schichten hergestellt (s. exp. Teil). Zur Ermittlung der pH-Werte der Schicht wurden nun pH-Messungen (s. exp. Teil) durchgeführt, was naturgemäß nur in wäßrigen Suspensionen des Schichtmaterials möglich ist. Eine Suspension stellt gegenüber einer zur Chromatographie vorbereiteten Schicht ein wesentlich verdünnteres System dar. Zur Untersuchung des Einflusses der Verdünnung auf den pH-Wert des mit Natronlauge imprägnierten Kieselgels wurde in Suspensionen verschiedener Konzentration gemessen, um aus dem dabei ermittelten Verhalten Rückschlüsse auf den in der Schicht vorliegenden pH-Wert ziehen zu können. Dabei wurde erwartungsgemäß festgestellt, daß sich aus der starken Base Natriumhydroxid und der schwachen Säure Kieselgel ein Puffersystem ausbildet. Ein solches Puffersystem ist nun in der Regel nicht nur dadurch charakterisiert, daß beim Zusatz relativ großer Mengen an Säure oder Base keine oder nur eine relativ geringe Änderung des pH-Wertes auftritt, sondern auch dadurch, daß es auch bei Verdünnung relativ pH-stabil bleibt. Dieses Verhalten läßt sich durch Messungen an Suspensionen verschiedener Konzentration nachweisen. Es kann, ausgehend von einer 30 proz. Suspension (s. exp. Teil) eine Verdünnung auf das 448-fache Volumen vorgenommen werden, ohne daß nennenswerte pH-Änderungen auftreten. Daher gelten die Suspensions-pH-Werte auch für die Schicht.

Die Messungen ergaben für die zur Chromatographie geeigneten Kieselgel H-Schichten der Konzentration 0,5–1,25*N* folgende pH-Werte:

NaOH-Konz., <i>N</i>	0,5	0,75	1	1,25
pH-Wert etwa	10,1	10,6	11,0	11,3

*Uniform saure Schichten.* Analog zu den alkalischen Schichten wurden nun uniforme, saure Schichten mit Hilfe von verschiedenen konzentrierten Lösungen von Schwefelsäure hergestellt (s. exp. Teil) und ebenfalls pH-Messungen an Suspensionen verschiedener Konzentration durchgeführt. Es konnte dabei festgestellt werden, daß die Gleichung  $\text{pH} = -\log(\text{H}^+)$  für das hier vorliegende System (Kieselgel + starke Säure) für die betreffenden Säurekonzentrationen strenge Gültigkeit besitzt und, daß sich daher anhand dieser Beziehung bei bekanntem Wassergehalt der Sorptionsmittelschicht eine Abschätzung des dort vorliegenden pH-Werts durchführen läßt.

Die Wasseraufnahme wurde bei orientierenden Versuchen gravimetrisch verfolgt.

Zur exakteren Beobachtung und Bestimmung der Wasseraufnahme wurde im Folgenden die Karl Fischer-Titration eingesetzt. Dabei wurde festgestellt, daß nach etwa 15 min, einem Zeitraum, den man für die Vorbereitung einer Platte zur Chromatographie in Rechnung stellen kann, bereits der Ausgleich mit der Atmosphäre bzgl. des Wassergehalts erfolgt ist. Es ist allgemein bekannt, daß der Wassergehalt der Kieselgel-Schichten von der jeweiligen relativen Luftfeuchtigkeit abhängt. Um nun einen Überblick über die möglichen Schwankungen bei verschiedenen relativen Feuchten zu erhalten, mit dem Ziel der Ermittlung eines geeigneten Durchschnittswertes, wurden diese Versuche über einen längeren Zeitraum hinweg bei verschiedenen klimatischen Bedingungen durchgeführt. Für alle mit der Atmosphäre im Gleichgewicht stehenden Kieselgel-Schichten (saure, basische und auch Schichten ohne spezielle Imprägnierung) wurden in Übereinstimmung mit den Ergebnissen anderer Autoren<sup>20,21</sup> Wassergehalte zwischen 8,5 und 15 Gew. % gefunden. Als Berechnungsgrundlage wurde daher ein Wassergehalt von 10% angenommen.

Für die uniform sauren Kieselgel-Schichten ergaben sich folgende Werte:

Konz. an Schwefelsäure, <i>N</i>	0,5	0,75	1,0
pH der 30 proz. Susp.	0,8	0,6	0,5
pH der Schicht	-0,6	-0,8	-0,9

Diese Abschätzung zeigt zusammen mit den Ergebnissen der alkalischen Schichten, daß für eine z.B. mit 0,5*N* Schwefelsäure und 0,5*N* Natronlauge in den angegebenen Mengenverhältnissen (s. exp. Teil) unter Verwendung von Kieselgel H hergestellte Gradient-Schicht ein pH-Bereich von etwa -0,6 bis etwa +10,1 zu erwarten wäre.

#### *Versuche zur Herstellung von pH-Gradient-Schichten mit Kieselgel H*

Es wurde nun versucht, mit Kieselgel H pH-Gradient-Schichten herzustellen. Dabei wurden mit den Säure- und Basekonzentrationen 0,1; 0,3 und 0,5*N ca.* 25 Versuche unternommen, wobei die Menge des Sorptionsmittels, der Säure und Base und vor allem das Verhältnis der Anteile von Säure und Base zu der Sorptionsmittelmengemenge in einem weiten Bereich variiert wurden. Es konnte bei all diesen Versuchen jedoch keine brauchbare Vorschrift ermittelt werden. Es war dabei oft der Fall, daß beim Arbeiten mit gleichen Mengenverhältnissen von Sorptionsmittel und Säure, bzw. Base einmal fünf Platten beschichtet werden konnten, während in anderen Fällen die Suspension nur zum Teil ausgestrichen werden konnte. Außerdem wurde festgestellt, daß die Schichten bei allen Versuchen sehr langsam und ungleichmäßig "auftröckneten", und zwar erfolgt dieser Vorgang bei den fünf Schichten einer Charge in der Reihenfolge 5,4,3,2,1. Weiterhin verläuft auch das Auftrocknen jeder einzelnen Schicht senkrecht zur Ausstreichrichtung sehr ungleichmäßig, und zwar trocknet die Schicht von der basischen Seite bis etwa zur Mitte recht schnell, dann folgt die Randzone der sauren Seite, während das Auftrocknen im Bereich dazwischen sehr viel langsamer vor sich geht. Die Zeit vom Ausstreichen bis zu dem Zeitpunkt, zu dem die gesamte Schicht den wäßrigen Glanz verlor, betrug in einigen Fällen um 15 min, meist aber wesentlich mehr (bis zu 1 Std.).

### *Prüfung des Gradient-Verlaufes auf Kontinuirlichkeit*

Zu diesem Zweck wurden verschiedene zweifarbige Säure-Base-Indikatoren strichförmig auf die Schicht aufgespritzt. Als besonders gut geeignet zur Kontrolle erwiesen sich Bromphenolblau und auch Bromchlorphenolblau (jeweils 1 proz. Lösungen in Methanol) mit einem Umschlag von intensivem Gelb nach Blau. Auf einer fehlerfreien pH-Gradient-Schicht muß der Indikator einen kontinuierlichen Farbübergang zeigen; und es muß sich dann bei der chromatographischen Entwicklung ein kontinuierlicher, scharf ausgebildeter Kurvenzug ergeben (vgl. Abb. 2b).

Mit dieser Testmethode wurden an den mit Kieselgel H hergestellten Schichten meist Fehler im mittleren Bereich festgestellt, zu erkennen am abwechselnden Auftreten von gelben und blauen Zonen im Indikatorstrich. Bei der Chromatographie des Indikators bildet sich dann kein stetiger Kurvenzug aus, sondern es treten im betreffenden Gebiet Zacken auf. Weiterhin wurde beobachtet, daß der Kurvenzug in der gesamten Zone, die am langsamsten aufgetrocknet war, denselben  $h_{RF}$ -Wert aufwies. Daraus folgt, daß in diesem Gebiet ein unerwünschter pH-Ausgleich stattfindet.

Die Versuche mit Kieselgel H verliefen also nicht befriedigend. Als entscheidendes Hindernis trat das langsame und ungleichmäßige Auftrocknen auf. In der Hoffnung, mit dem schnell "aufdrocknenden" Kieselgel G bessere Resultate zu erzielen, wurden die vorstehend beschriebenen Versuche nun wiederholt.

### *Versuche mit Kieselgel G*

*Herstellung von Gradient-Schichten mit Kieselgel G.* Nach den Erfahrungen mit Kieselgel H wurde hier eine andere Vorgehensweise gewählt: Es wurde zuerst festgestellt, ob und unter welchen Bedingungen brauchbare pH-Gradient-Schichten bereitet werden konnten, bevor Versuche zur Charakterisierung unternommen wurden.

Für die Herstellung von Gradient-Schichten mit den Konzentrationen 0,1; 0,3 und 0,5*N* Säure und Base wurden Vorschriften ermittelt (s. exp. Teil). Die danach bereiteten Schichten trocknen schnell und gleichmäßig auf und die pH-Änderung erweist sich bei einer Prüfung des Gradient-Verlaufes als kontinuierlich. Versuche mit der Konzentration 0,75*N* schlugen dagegen fehl: Obwohl die Einzelsuspensionen sehr dünnflüssig waren, blieb die Gesamtsuspension beim Ausstreichversuch im mittleren Bereich in ca. 10 cm Breite an der Mischwelle hängen. Es wurde weiterhin untersucht, ob alle 5 Schichten eines Streichvorganges denselben pH-Gradient aufweisen und keine Verschiebung senkrecht zur Ausstreichrichtung erfolgt. Dazu kann man z.B. alle 5 noch feuchten Schichten mit Universalindikator-Lösung besprühen;<sup>7</sup> man kann zur Kontrolle aber auch pH-Messungen durchführen und zwar am sinnvollsten an der ersten und letzten Schicht einer Charge. Dabei wurden von den Schichten, auf der sauren Seite beginnend, über die gesamte Plattenbreite 19 Proben genommen und die pH-Messung an 2,5 proz. Suspensionen vorgenommen. Wie dabei festgestellt werden konnte, besteht zwischen dem Gradient Verlauf der ersten und letzten Schicht einer Charge kein Unterschied.

*Ermittlung der pH-Intervall-Grenzen.* Auch hier wurden uniform alkalische und saure Schichten hergestellt, und zwar mit den Konzentrationen 0,1; 0,3 und 0,5*N* (s. exp. Teil). Alle Schichten waren zur Chromatographie verwendbar.

Es ergaben sich folgende Schicht-pH-Werte

Konz. an NaOH, <i>N</i>	0,1	0,3	0,5
pH-Wert etwa	7,7	8,4	9,0
Konz. an H <sub>2</sub> SO <sub>4</sub> , <i>N</i>	0,1	0,3	0,5
pH der 30 proz. Susp.	2,3	1,5	0,8
pH der Schicht	0,9	0,1	-0,6

*Charakterisierung der pH-Gradient-Schichten.* Zur Abschätzung des Gradient-Verlaufs in der Schicht wurden nun an verschiedenen konzentrierten Suspensionen des Schichtmaterials der Gradient-Schichten pH-Messungen vorgenommen. Für den sauren Bereich wurden den gemessenen Werten wiederum die pH-Werte gegenübergestellt, die sich mit dem Meßwert für die konzentrierteste Suspension als angenommene Basis unter Beachtung der Verdünnung berechnen lassen. Aus dem Vergleich dieser beiden Größen ergibt sich, bis zu welcher Plattenbreite von der sauren Seite her gerechnet die Beziehung  $\text{pH} = -\log [\text{H}^+]$  Gültigkeit hat und, wie der pH-Verlauf der Schicht im Vergleich zu der Kurve  $\text{pH} = f(\text{Plattenbreite})$  für die konzentrierteste Suspension (28%) etwa aussehen muß. Im Gültigkeitsbereich der pH-Konzentrations-Beziehung muß die Kurve der Schicht um den Logarithmus der Verdünnung der 28 proz. Suspension gegenüber der Schicht unter der Kurve für die Suspension liegen. Dort, wo die Beziehung keine Gültigkeit mehr hat, muß die Schicht-pH-Kurve in entsprechendem Maße an die Suspensions-pH-Kurve angenähert werden und im Neutralpunkt dann in diese übergehen. Im alkalischen Bereich sind beide Kurven aufgrund des Pufferverhaltens identisch.

Aus den einzelnen Kurven (vgl. Abb. 1) ergeben sich für die Gradient-Schichten der drei Konzentrationen folgende pH-Intervalle:

Konz. an H <sub>2</sub> SO <sub>4</sub> und NaOH, <i>N</i>	0,1	0,3	0,5
Plattenbreite, mm	10 190	10 190	10 190
pH-Werte	4,3 7,7	0,5 8,3	-0,2 8,9

Die Hell-Dunkel-Streifen über den Kurven in Abb. 1 stellen Ausschnitte aus Photographien dar, die von den mit Kieselgel GF<sub>254</sub> hergestellten pH-Gradient-Schichten der drei verschiedenen Konzentrationen im UV-Durchlicht aufgenommen wurden. Wie auf Seite 8 gezeigt wird, kann mittels eines säureempfindlichen Fluoreszenzindikators eine Kontrolle der pH-Gradient-Schichten durchgeführt werden.

*Kontrolle der pH-Gradient-Schichten.* Mit Bromphenolblau: Für einwandfreie Schichten der verschiedenen Konzentrationen lassen sich folgende Sollwerte festlegen, wobei die Farbumschläge bei höherer Konzentration der Imprägnierung erwartungsgemäß schärfer ausgebildet werden und daher besser wahrzunehmen sind. Im Folgenden sind zur Charakterisierung der Schichten nur die Bereiche angegeben, in denen die Indikatorfarben dem Auge rein erscheinen. In den Zonen dazwischen tritt jeweils eine Mischfarbe aus Gelb und Blau auf.

Konz. 0,5*N*: Bis 68–71 mm vom sauren Rand der Glasplatte liegt ein reines Gelb, von etwa 90–95 mm ab liegt reines Blau vor.

Konz. 0,3*N*: Bis zu 42–47 mm ist reines Gelb, ab 85–90 mm reines Blau zu erkennen.

Konz. 0,1N: Auf diesen Schichten ist kein reines Gelb mehr wahrzunehmen. Als Kriterium kann dienen, daß ab etwa 80 mm nur noch Blau zu erkennen ist.

Bei Verwendung von Kieselgel GF<sub>254</sub> anhand des Fluoreszenzindikators, der durch Säure zerstört wird, was eine Fluoreszenzlöschung, bzw. -minderung zur Folge hat (vgl. Abb. 1).

Konz. 0,5N: Die Fluoreszenzlöschung erstreckt sich bis 80–85 mm vom sauren Plattenrand, was einem pH-Intervall von 4,5–5,0 entspricht.

Konz. 0,3N: Bis etwa 45 mm vom sauren Rand tritt Fluoreszenzlöschung auf, bis ca. 70 mm ist die Fluoreszenz dann noch ganz schwach vermindert. Der Abstand von 70 mm entspricht einem pH-Wert von etwa 5,3.

Konz. 0,1N: Bis etwa 25–30 mm vom sauren Rand zeigt sich eine leichte Fluoreszenzminderung. Dieser Abstand entspricht etwa einem pH von 4,5.

Damit waren nun pH-Gradient-Schichten mit definierter Gradient-Ausbildung reproduzierbar herstellbar; es konnte also nun jedem Schichtbereich erstmals ein pH-Wert zugeordnet werden. Es muß allerdings betont werden, daß reproduzierbare Ergebnisse nur erhalten werden, wenn die Herstellung der Schichten streng nach der im exp. Teil gegebenen Vorschrift erfolgt.

#### TYPISCHE KURVENFORMEN BEI DER CHROMATOGRAPHIE IM pH-T-GRADIENT

Mit der Aufstellung der für die verschiedenen pH-Gradient-Schichten gültigen pH-Orts-Kurven war die Voraussetzung geschaffen, systematische Untersuchungen über das chromatographische Verhalten verschiedener Substanzklassen durchzuführen. Von Interesse waren alle Verbindungen, die im pH-Intervall der Schichten zu einer Reaktion mit der Schichtimpregnierung befähigt sind. Zur Erstellung eines pH-T-Chromatogrammes wird die Probelösung in Form einer sich über die ganze Breite einer Schicht erstreckenden strichförmigen Startzone aufgegeben. Um uns ein mühsames und zeitraubendes manuelles Aufpunkten zu ersparen, entwickelten wir in Zusammenarbeit mit der Fa. Desaga, den a.a.O.<sup>22,23</sup> beschriebenen "Autoliner", ein Gerät für das vollautomatische Auftragen von Probelösungen in Band- oder Strichform zur analytisch-qualitativen, mikropräparativen und quantitativen DC, PC und Elektrophorese. Zur Chromatographie wurden vorzugsweise 375 µm dick ausgestrichene Schichten verwandt.

Im Laufe unserer Untersuchungen<sup>23</sup> fanden wir insgesamt 6 prinzipiell verschiedene Kurvenformen, die in Abb. 2 a–f schematisch zusammengestellt sind.

Eine detaillierte Besprechung einzelner Anwendungsbeispiele soll in einer späteren Arbeit vorgenommen werden.

#### EXPERIMENTELLER TEIL

##### *Kieselgel H: Uniform alkalische Schichten*

Die Suspensionen wurden aus 30,0 g Kieselgel HF<sub>254</sub> nach Stahl für die DC der Firma Merck AG, Darmstadt, und 62,0 ml der jeweiligen Natriumhydroxid-Lösung bereitet.

*pH-Messungen.* Zu Beginn der pH-Messungen wurde folgender Vergleich durchgeführt: (a) Die Kieselgel-Suspension wurde ca. 3 min mit einem Magnetrührer gut durchmischt, das Sorptionsmittel abzentrifugiert, und die pH-Messung in der abdekantierten überstehenden Lösung vorgenommen. (b) Zur pH-Messung wurde unmittelbar die gut durchmischte Suspension verwandt. Da die nach beiden Methoden ermittelten Werte identisch waren, wurden alle späteren Messungen direkt in der Suspension vorgenommen.

*Zusammensetzung der Suspensionen zur pH-Messung.* Man versteht üblicherweise unter einer 10 proz. Suspension, daß der Anteil des Feststoffes 10% des Gesamtgewichtes der Suspension beträgt. Zur Durchführung der Messungen wurden kleine Kunststoffbecher verwandt, deren Fassungsvermögen einem Suspensionsgewicht von ca. 12 g entsprach. Daher wurde z.B. die konzentrierteste



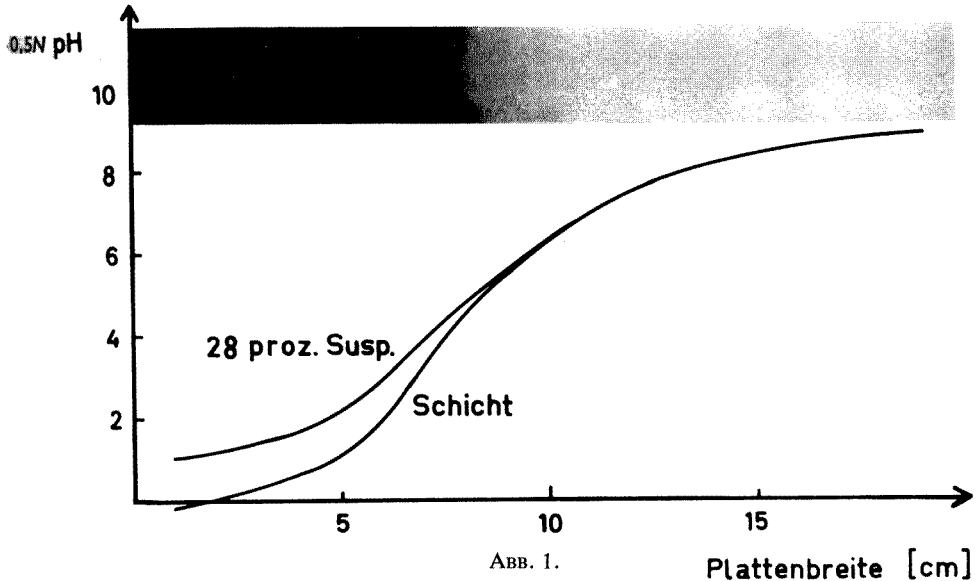
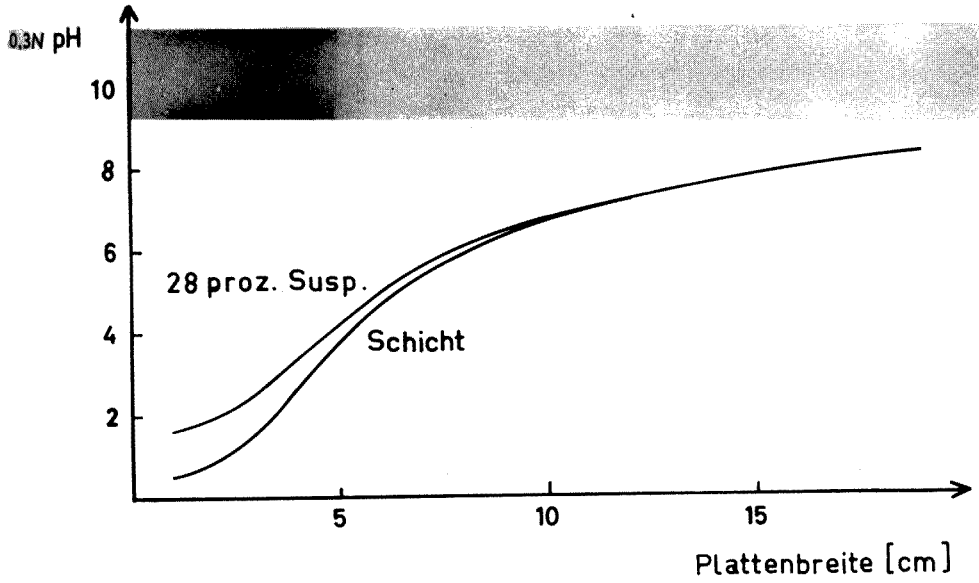
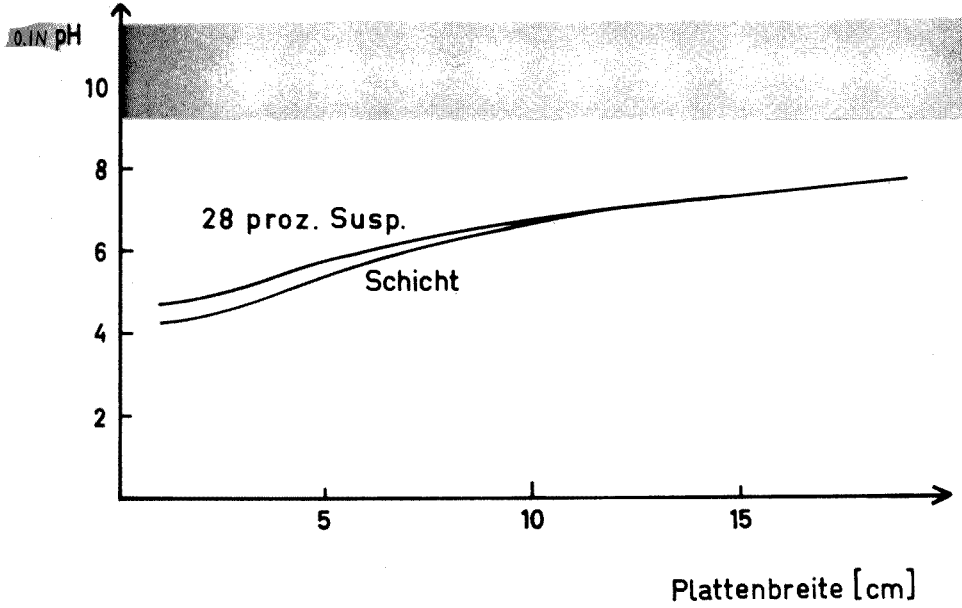


ABB. 1.

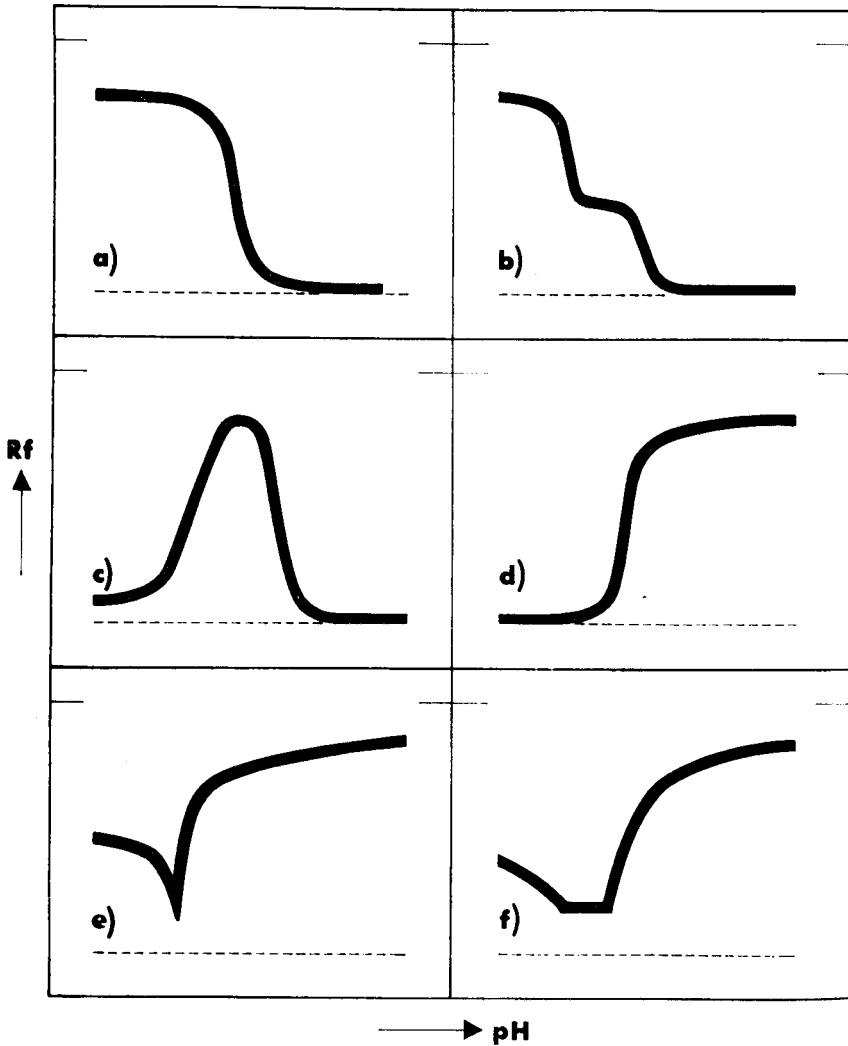


ABB. 2

ABB. 2a.—Einbasige Säuren: Der Wendepunkt im Bereich des steilen Anstiegs der Kurve entspricht dem "pK<sub>s</sub>-Wert"\* der Säure. Links davon zum sauren Rand der Schicht hin wird die freie Säure nur relativ schwach adsorbiert, während das rechts vom "pK<sub>s</sub>-Wert" vorliegende Natriumsalz stark adsorbiert wird.

ABB. 2b.—Zweibasige Säuren: Hier gilt Entsprechendes wie bei a): Am höchsten im Chromatogramm liegt die Verbindung mit zwei sauren Gruppen; dann folgt nach einem dem ersten pK<sub>s</sub>-Wert entsprechenden Abfall der Kurve der Bereich des Mononatriumsalzes und nach einem zweiten pK<sub>s</sub>-Wert am weitesten unten im Chromatogramm das Diantriumsalsz.

ABB. 2c.—Diesen Kurvenverlauf fanden wir bei verschiedenen Ampholyten: Stark adsorbiert werden das einfach positiv geladene Ammoniumion im sauren Chromatogrammbereich sowie das einfach negativ geladene Carboxylat-Anion im basischen Bereich. Dazwischen liegt in der Umgebung des isoelektrischen Punktes mit hohem hR-Wert ein zwitterionisches, insgesamt elektroneutrales und daher relativ unpolares Molekül vor.

ABB. 2d.—Der steile Anstieg entspricht dem Übergang des protoniertenamins, also eines stark adsorbierten Ammoniumions, in das freie unpolare Amin.

ABB. 2e.—Diese Kurvenform wurde für die Gruppe der Opium-Alkaloide erhalten.

ABB. 2f.—Dieses Verhalten fanden wir bei den Tropa-Alkaloiden.

\* Es ist dabei die Einschränkung zu machen, daß es sich bei der Schicht um ein wasserarmes System handelt.

(30 Proz.) Suspension bei der Messung der uniformen Schichten aus 3,60 g imprägniertem Kieselgel und 8,40 g (ml) Wasser bereitet. Zur Durchmischung wurde ein Magnetrührer benutzt.

#### Kieselgel H: Uniform saure Schichten

Es wurden auf je 30,0 g Kieselgel HF<sub>254</sub> für die DC 62,0 ml der 0,5N bzw. 0,75N Schwefelsäure eingesetzt, während im Falle der 1N Schwefelsäure 65,0 ml ge braucht wurden.

Der Wassergehalt wurde nach Karl Fischer bestimmt.

#### Herstellung von pH-Gradient-Schichten mit Kieselgel GF<sub>254</sub>

*Vorbereitung des Streichvorganges.* In zwei 100 ml-Weithals-Erlenmeyer-Kolben gleicher Form werden gleiche Mengen an Kieselgel GF<sub>254</sub> eingewogen. Die Gefäße sollen gleich sein, damit beim Eingeben der Suspension in die Diagonaleiterräume bei etwa gleicher Viskosität gleiche Volumina aus den Erlenmeyerkolben ausfließen. Bei der Ermittlung der Arbeitsvorschriften wurden diese Volumina durch Eingießen in Meßzylinder bei den verschiedenen Konzentrationen und Schichtdicken jeweils überprüft. Der GM-Streicher wird betriebsbereit auf die Ansatzplatte gelegt. Säure und Base werden aus den Büretten in 2 Gefäße gleicher Form, z.B. Meßzylinder abgemessen. Aufebene eine Lage der Trägerplatten auf der Arbeitsschablone (Wasserwaage) ist besonderer Wert zu legen, um eine Verschiebung im Gradient beim Antrocknen der Schicht zu vermeiden. Es empfiehlt sich daher, eine geeignete Stelle des Labortisches für die Arbeitsschablone auszusuchen. Weiterhin ist auf dichten Sitz des Bodenblechs in den Führungen und des Diagonalteilers im Teilertrug zu achten.

*Eigentlicher Streichvorgang.* Zu dem in zwei 100-ml-Erlenmeyer-Kolben eingewogenen Sorptionsmittel werden abgemessene Mengen an Schwefelsäure, bzw. Natronlauge gegeben. Die Kolben werden gut verschlossen und unter Festhalten der Stopfen ca. 10 sek intensiv geschüttelt. (Das Festhalten der Stopfen ist notwendig, weil beim Versetzen des Kieselgels mit Säure und Lauge etwas Wärme frei wird.)

Die Suspensionen werden an den Enden des Teilertrugs gleichzeitig eingegeben und dann in den engen Teilerabschnitten mit einem jeweils sauberen Spatel auf gleiches Niveau gebracht.

Die Diagonal-Trennwand wird nun vorsichtig herausgehoben.

Sofort anschließend werden die Einzelsuspensionen durch Herausziehen des Bodenblechs in die Mischerhülse eingegeben.

Es wird 8–10 sek nur in einer Richtung gemischt, wobei die Mischwelle entgegengesetzt der Ausstreichrichtung rotiert.

Die Mischerhülse wird anschließend am Hebel so weit gedreht, bis dieser senkrecht steht, und die Suspension in dieser Stellung ausgestrichen. Bei dieser Hebelstellung kann Luft von oben nachströmen. Ein Ausstreichen bei waagerechter Stellung des Hebels ist nicht möglich, da durch den Einbau der Mischwelle durch das bei waagerechter Stellung des Hebels geöffnete Luftloch nur die nächstgelegene Kammer belüftet würde.

Für das Arbeiten mit Kieselgel GF<sub>254</sub> für die DC wurden folgende Vorschriften ermittelt:

Schichtdicke, <i>µm</i>	Konz. an H <sub>2</sub> SO <sub>4</sub> bzw. NaOH, N	Zusammensetzung der Suspension		Antrockenzeit, <i>min</i>
		K-gel, g	Säure bzw. Base, ml	
250	0,1	18,0	36,0	7–8
	0,3	18,0	37,0	5–7
	0,5	18,0	38,5	3–5
375	0,1	22,0	44,0	7–8
	0,3	22,0	45,0	5–7
	0,5	22,0	47,0	3–5

Die Schichten wurden bis zum Verschwinden des wäßrigen Glanzes (Antrockenzeit) auf der Schablone liegen gelassen, dann im Warmluftstrom solange getrocknet, ca. 15 min bis die Transparenz verschwunden ist und die Oberfläche rein weiß geworden ist, und anschließend etwa 40 min auf 110° erhitzt.

Versuche mit 0,75N Schwefelsäure bzw. Natronlauge. Es wurden jeweils 22,0 g Kieselgel G mit 49,0 ml Säure bzw. Base suspendiert.

#### Kieselgel G: Bereitung der uniformen Schichten

Die bei der Herstellung von Gradient-Schichten eingesetzten Säure-, bzw. Basemengen wurden auf je 25,0 g Kieselgel G umgerechnet; es wurden also 50,0 ml 0,1N, 51,20 ml 0,3N und 53,40 ml 0,5N Säure, bzw. Base verwandt.

*Allgemeines zur Dünnschicht-Chromatographie*

Geräte: Es wurde die Grundausrüstung zur DC der Fa. Desaga, Heidelberg, benutzt. Zur Herstellung der Gradient-Schichten auf  $200 \times 200$  mm Platten diente ein modifizierter GM-Streicher nach Stahl.<sup>1</sup>

Fließmittel: Je nach Trennproblem wechselnde Gemische von Chloroform und Methanol (Reinheitsgrad "zur Analyse").

**Summary**—The possibilities and present applications of gradient thin-layer chromatography are summarized. Methods for the preparation of reproducible and fault-free pH-gradient layers are given. These layers may be characterized by the relationship between pH and position, so that for the first time layers may be produced with a definite gradient profile. Finally, the typical shapes of curves for some classes of compounds after pH-traverse-gradient chromatography are summarized and briefly explained.

**Résumé**—On résume les possibilités et les applications actuelles de la chromatographie en couche mince à gradient. On donne des méthodes pour la préparation de couches à gradient de pH reproductibles et exemptes de défaut. Ces couches peuvent être caractérisées par la relation entre le pH et la position, de sorte que pour la première fois on peut produire des couches avec un profil de gradient défini. Finalement, on résume et explique brièvement les silhouettes typiques de courbes pour quelques classes de composés après chromatographie avec gradient de pH.

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## ION-EXCHANGE SEPARATION OF VANADIUM, ZIRCONIUM, TITANIUM, MOLYBDENUM, TUNGSTEN AND NIOBIUM

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**Summary**—Schemes for the separation of two or more of the elements vanadium, zirconium and/or titanium, molybdenum and tungsten from each other and from relatively large amounts of niobium have been developed, a strongly basic anion-exchange resin being used. Interference from niobium is avoided by using hydrofluoric acid to elute vanadium, zirconium, titanium and molybdenum. The application of coupled columns to improve the efficiency of separation of multi-component mixtures is demonstrated. The use of an "interval" equation defining the volume interval between successively eluted solutes is proposed for calculating the column length required for a particular separation. This equation is especially useful for determining the extent to which a column must be lengthened when overlapping occurs because of high column loading.

In a previous paper, an anion-exchange method for the analysis of niobium alloys was described.<sup>1</sup> Appropriate concentrations of hydrofluoric acid were used for the separate elution of V, Zr (and/or Ti, Hf) and Mo. The W, Nb and Ta remaining on the column were then separated with hydrochloric-hydrofluoric acid mixtures. There was no interference from relatively large amounts of Nb.

In the present paper, the same approach is used to develop ion-exchange schemes for the separation of all possible combinations of two or more of the elements V, Zr and/or Ti, Mo and W from each other and from relatively large amounts of Nb. Coupled columns are used to resolve complex mixtures. The effect of high column loading on the separation of V and Zr is evaluated to establish the optimum combination of column length and hydrofluoric acid concentration for the initial separation of V.

The use of "interval" equations defining the volume interval between successively eluted solutes is proposed for calculating the column length required for a particular separation and for determining the extent to which a column must be lengthened when overlapping occurs because of high column loading.

### EXPERIMENTAL

#### *General procedure*

Polystyrene tubing 25 mm in diameter was used to prepare the columns of 270-mesh Dowex-1 resin (8-10% cross-linkage). The interstitial volume was found<sup>2</sup> to be 46% of the bed volume and the capacity 1.5 mequiv per ml of bed volume or 0.76 mequiv per mm of column length.

Solutions of the elements used were prepared by dissolving the pure metals in a mixture of hydrofluoric and nitric acids in Teflon beakers, evaporating to dryness and dissolving the residue in dilute hydrofluoric acid. The resulting solutions were transferred to appropriate preconditioned columns and collection of 25-ml fractions was begun with the addition of the sample, at a flow-rate of 2.5 ml/min (0.5 ml/cm<sup>2</sup>/min), which is relatively slow and typical of that used in other ion-exchange investigations.<sup>3</sup>

TABLE I.—SEMI-QUANTITATIVE CHEMICAL TESTS

Element	Treatment	Positive	Least amount detectable, mg/25 ml
V	To 10 ml add 0.5 ml of H <sub>2</sub> SO <sub>4</sub> plus 3–4 drops of HNO <sub>3</sub> . Heat to appearance of heavy SO <sub>3</sub> fumes. Add 3 drops of 30% H <sub>2</sub> O <sub>2</sub> .	Brown colour	~0.1
Zr	To 10 ml add 4 ml of HClO <sub>4</sub> plus 3–4 drops of HNO <sub>3</sub> . Heat to appearance of heavy HClO <sub>4</sub> fumes and fume for 1 min. Transfer to small Pyrex beaker and fume just to dryness. Add 8 ml of H <sub>2</sub> O and 3 ml of HCl, heat, then add 5 ml of 0.1% Alizarin Red S solution.	Red colour	~0.1
Ti	To 5 ml add 1 ml of H <sub>2</sub> SO <sub>4</sub> plus 3–4 drops of HNO <sub>3</sub> . Heat to appearance of heavy SO <sub>3</sub> fumes. Add 9 ml of H <sub>2</sub> O and 3 drops of 30% H <sub>2</sub> O <sub>2</sub> .	Yellow colour	<0.1
Mo	To 5 ml add 4 ml of 25% SnCl <sub>2</sub> solution and 2 ml of 10% NaSCN solution.	Red-brown colour	~0.3
W	To 20 ml add 0.5 ml of H <sub>2</sub> SO <sub>4</sub> . Heat to appearance of heavy SO <sub>3</sub> fumes. Add 2 ml of H <sub>2</sub> O and 3 ml of 25% SnCl <sub>2</sub> solution.	Blue precipitate	~0.3
Nb	To 5 ml add 0.5 ml of H <sub>2</sub> SO <sub>4</sub> . Heat to appearance of heavy SO <sub>3</sub> fumes. Add 3 ml of H <sub>2</sub> O and 3 ml of NH <sub>4</sub> OH.	White precipitate	~0.3

TABLE II.—REAGENTS USED IN PHOTOMETRIC QUANTITATIVE TESTS

Element	Reagent	Medium
V	H <sub>2</sub> O <sub>2</sub>	20% H <sub>2</sub> SO <sub>4</sub>
Zr	Xylenol Orange	0.5% H <sub>2</sub> SO <sub>4</sub>
Ti	H <sub>2</sub> O <sub>2</sub>	10% H <sub>2</sub> SO <sub>4</sub>
Mo	H <sub>2</sub> O <sub>2</sub>	10% HClO <sub>4</sub> –10% H <sub>3</sub> PO <sub>4</sub>
W	NaSCN	50% HCl

The elution behaviour of the elements was determined by analysing these fractions, photometrically for quantitative results, and by spot-tests with visual comparison for semi-quantitative. The tests used are listed in Tables I and II.

The tests in Table I were applied as written, to locate the beginning and end of each elution peak; smaller portions were taken for other tests. In the case of V and Nb, fuming was omitted for initial location of the peaks. For fractions where V and Ti might be present together, hydrofluoric acid was added after the peroxide, to mask the Ti and reveal V.

In the separation studies the amount of Nb taken was generally enough to provide a total of 1 g of mixture. This sample size was selected as convenient for practical analytical applications.

The use of concentrated hydrofluoric acid solutions may be considered by some to present a problem. All ion-exchange work in this laboratory is performed in a chemical hood constructed of clear plastic. Samples are prepared in an adjacent hood. If appropriate precautions are taken these methods can be employed with no difficulty.

#### Separation of vanadium

In the original method<sup>1</sup> 13*M* hydrofluoric acid was used for the initial separation of V from Zr or Ti. Approximately 700 ml of eluent are required to remove V completely from a 200-mm column. Under these conditions V and Zr are just barely separated. At higher acid concentrations the distribution coefficients of these two elements become closer and with 20*M* hydrofluoric acid the elution peaks almost coincide. At lower acid concentrations, the distribution coefficient of Zr increases

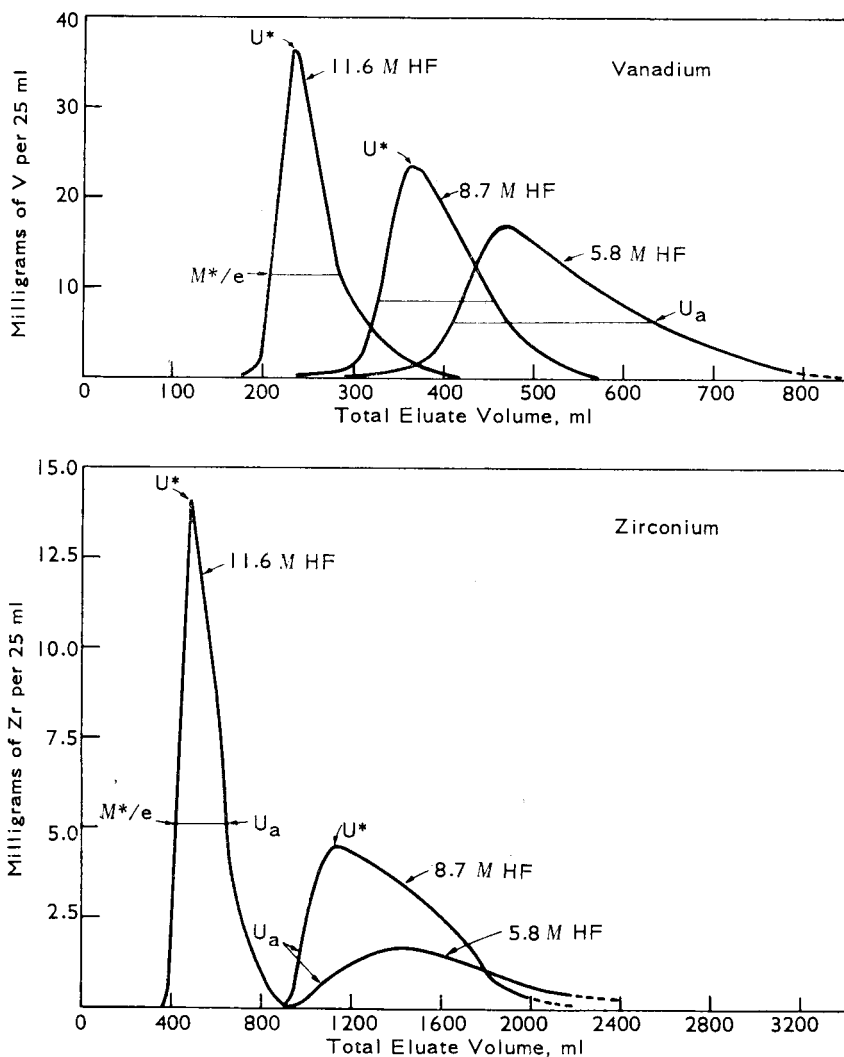


FIG. 1.—Elution of vanadium and zirconium.  
 Column dimensions:  
 vanadium—110 mm  $\times$  500 mm<sup>2</sup>;  
 zirconium—11.6 and 8.7M HF,  
 110 mm  $\times$  500 mm<sup>2</sup>; 5.8M HF, 38 mm  $\times$  500 mm<sup>2</sup>.

much more rapidly than that of V.<sup>4</sup> Thus with decreasing acid concentration, the separation factor (approximately equal to the ratio of the distribution coefficients) increases markedly while the elution rate of V decreases only a little. It should therefore be possible to realize greater efficiency in the separation of V by using lower acid concentrations and a shorter column. The minimum column length would depend on the effect of the load.

Column lengths theoretically required for the separation of V and Zr at low loading levels were calculated from the elution curves of these elements with 5.8, 8.7 and 11.6M hydrofluoric acid. The elution behaviour of Zr with 5.8M hydrofluoric acid was determined with a 38-mm column; the sample was 50 mg of Zr in 10 ml of 3M hydrofluoric acid. In every other case a 110-mm column was used and sample solutions contained 100 mg of the element. Column loading was thus <3% of the total column capacity, assuming singly-charged fluoride complexes to be the adsorbed species. The elution curves are shown in Fig. 1.

The column lengths were calculated according to Rieman and Sargent.<sup>2</sup> The pertinent equations are presented here for convenience.

The peak elution volume,  $U^*$ , of a given solute can be predicted from the expression

$$U^* = CV_1 + V_1 \quad (1)$$

where  $C$  is the distribution ratio of the solute between resin and interstitial liquid in a given theoretical plate at equilibrium, and  $V_1$  is the volume of the interstitial liquid phase of the column (in ml). When the distribution ratios of the solutes are independent of total solute concentration, *i.e.*, at concentrations  $<3\%$  of total column capacity,<sup>3</sup> the elution curves can be treated as being Gaussian. Rieman and Sargent combined the Gaussian equation with some of the equations of Mayer and Tompkins<sup>5</sup> to obtain a comparatively simple equation for the elution curve:

$$M = M^* \exp \left\{ \frac{-p}{2} \left( \frac{C+1}{C} \right) \left( \frac{U^* - U}{U^*} \right)^2 \right\} \quad (2)$$

where  $M$  is the concentration of solute eluted at eluate volume  $U$ ;  $M^*$  is the concentration of the solute at the peak elution volume  $U^*$ ; and  $p$  is the number of theoretical plates in the column.

TABLE III.—CALCULATED VALUES OF  $C$ ,  $P$  AND  $H$

[HF], $M$	Distribution ratios		Theoretical plates per mm of column		Required column length, $H$ , mm
	$C_v$	$C_{Zr}$	$P_v$	$P_{Zr}$	
5.8	17.3	157	0.141	0.88	29
8.7	12.5	41.3	0.225	1.61	53
11.6	7.7	17.5	0.240	1.30	130

If  $U_a$  is the value of  $U$  corresponding to a solute concentration of  $M^*/e$ , where  $e$  is the base of natural logarithms, the following expression for the number of plates is obtained:

$$p = \left( \frac{2C}{C+1} \right) \left( \frac{U^*}{U^* - U_a} \right)^2 \quad (3)$$

From equation (2) and a table of probability integrals, the length of column ( $H$  mm) required to provide a separation of two solutes with a cross-contamination of 0.05% can be calculated:

$$\sqrt{H} = \frac{3.29}{C_2 - C_1} \left( \frac{C_2 + 0.5}{\sqrt{P_2}} + \frac{C_1 + 0.5}{\sqrt{P_1}} \right) \quad (4)$$

where the subscripts 1 and 2 indicate the order of elution (*i.e.*,  $C_1 < C_2$ );  $P$  is the number of plates per mm of column. The value 3.29 is the number of standard deviations that set the limits of the 0.9995 probability integral. By substitution of other limit values, other degrees of cross-contamination can be allowed for.

An experimental elution curve provides two values for  $U_a$ , at the leading and trailing edges of the curve. If the elution follows equation (2) perfectly, both values of  $U_a$  will give the same value of  $p$  from equation (3). However, most experimental curves are subject to tailing; the  $p$  value corresponding to the smaller  $U_a$  may differ considerably from and will be larger than that obtained from the larger  $U_a$ .

Since the separation of two solutes is dependent on the trailing edge of the solute which elutes first and the leading edge of the next solute, the corresponding  $U_a$  values must be used to determine the column length required, *i.e.*,  $p_1$  is calculated from  $U_a$  for the trailing edge of the first peak and  $p_2$  from  $U_a$  for the leading edge of the next.

The column lengths required to separate V and Zr were calculated by means of equation (4) and increased by 10% to allow for experimental error, as recommended by Rieman and Sargent. The results are listed in Table III.

Although the plate theory is applicable only if column loading is kept low, Glueckauf<sup>6</sup> has shown that the allowable loading is dependent on the number of theoretical plates and that even 10% loading can be tolerated on a column having a small number of plates, *e.g.*, 200, as long as the column can satisfactorily separate trace amounts.

To evaluate the effect of the desired 1-g load level, 8.7M hydrofluoric acid was used to elute V and Zr from two columns loaded with 100 mg each of V, Zr, Mo and W, and 600 mg of Nb. One column was 60 mm long, the other 90 mm. Column loading was  $\sim 24$  and  $\sim 16\%$  respectively. The elution curves overlapped most on the 60-mm column. It was estimated that quantitative separation of V and Zr would require a column about 120 mm long with  $\sim 12\%$  loading.

If 12% is taken as the maximum allowable load, it should be possible to use an eluent of higher concentration to increase the elution rate of V, provided adequate separation from Zr could be expected at low load levels. The optimum hydrofluoric acid concentration must therefore be between



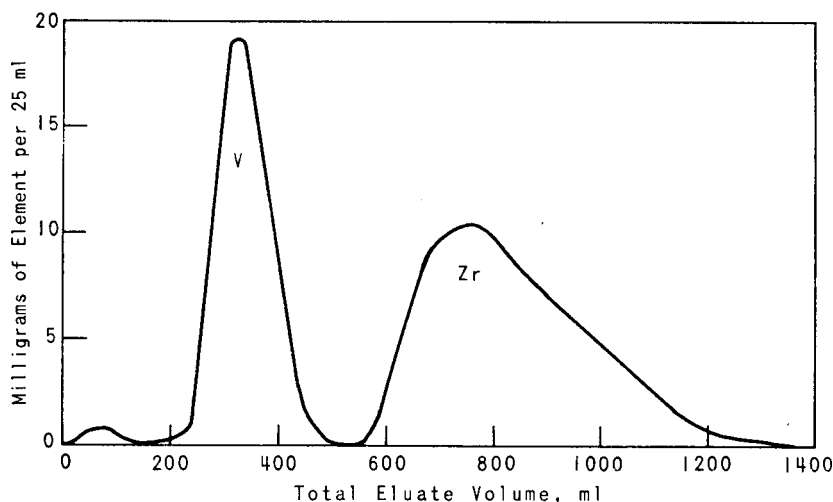


FIG. 2.—Separation of vanadium and zirconium with 10.1M HF on a 125 mm  $\times$  500 mm<sup>2</sup> column.

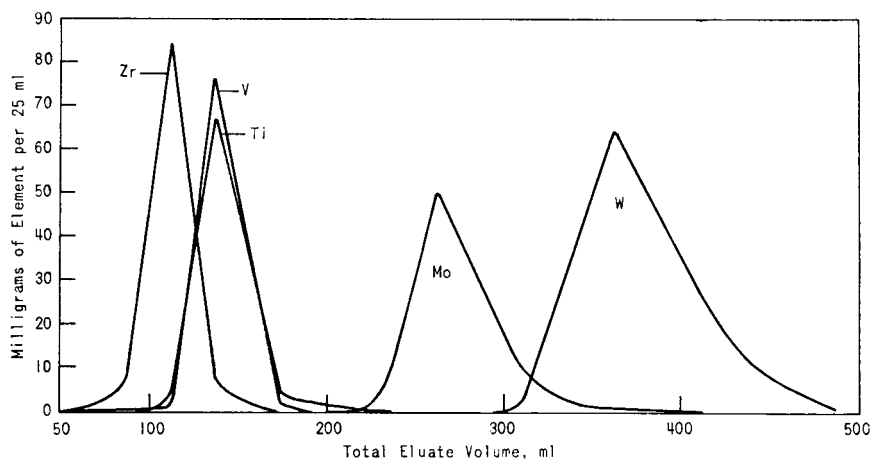


FIG. 3.—Superimposed individual elution curves obtained with 27.5M HF on a 110 mm  $\times$  500 mm<sup>2</sup> column.

8.7 and 11.6M. Figure 2 shows the results obtained with 10.1M hydrofluoric acid and a 125-mm column.

#### *Elution behaviour of the elements in 27.5M hydrofluoric acid*

Evaluation of the elution behaviour with 27.5M hydrofluoric acid was prompted by the distribution coefficient curves published by Faris.<sup>4</sup> The curves for Mo and W begin to diverge with increasing acid concentration above 15M. Should this trend persist with hydrofluoric acid  $>$  24M, the maximum used by Faris, the separation of Mo from W might be possible at higher acid concentration. Separation with 24M acid was very poor,  $\sim$ 90% of the W being eluted with Mo. Elution curves were therefore determined with 27.5M acid as eluent on 110-mm columns carrying 100 mg of V, Zr, Ti or Mo, or 200 mg of W, dissolved in 10 ml of 3M hydrofluoric acid, and are shown in Fig. 3. Obviously Mo and W can be separated with 27.5M hydrofluoric acid, and so can V and Zr or Ti from Mo. Mixtures of W with one of the elements V, Zr or Ti can be separated with 27.5M hydrofluoric acid on a 110-mm column, provided column loading is not excessive.<sup>1</sup>

The distribution ratios and number of theoretical plates were calculated and are listed in Table IV. They were used to calculate the column lengths needed to separate Ti and Mo (132 mm), and Mo and W (203 mm). The figures given include a 10% increase to allow for experimental error. A

TABLE IV.—CALCULATED VALUES OF *C* AND *P* IN 27.5*M* HF

	Zr	V	Ti	Mo	W
Distribution ratio	<i>C</i> 2.9	3.6	3.9	7.7	12.5
Theoretical plates per mm	<i>P<sub>r</sub></i> * —	1.28	0.77	2.14	2.02
	<i>P<sub>t</sub></i> * 0.44	0.46	0.39	0.58	—

\* *P<sub>r</sub>* is based on the *U<sub>a</sub>* value for the leading edge, *P<sub>t</sub>* on *U<sub>a</sub>* for the trailing edge.

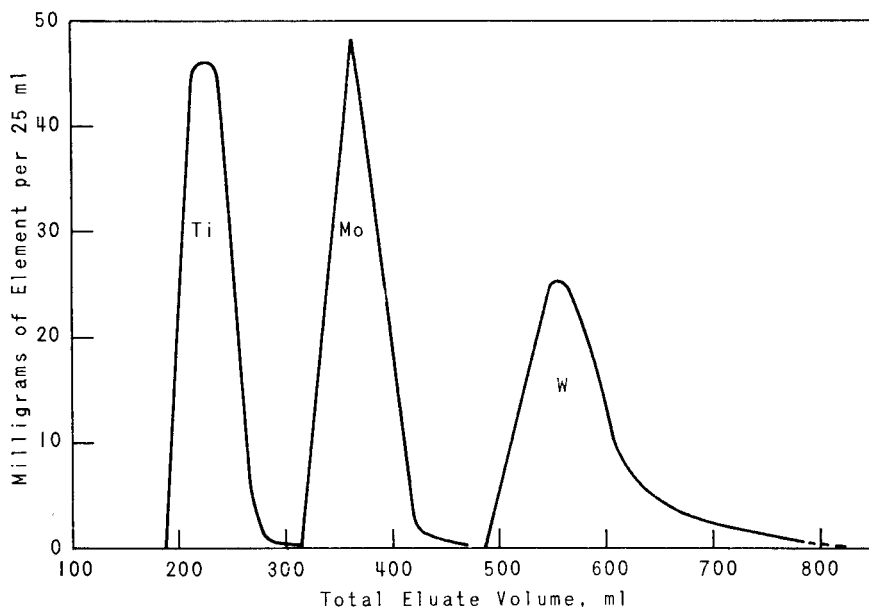


Fig. 4.—Separation of titanium, molybdenum and tungsten with 27.5*M* HF on a 210 mm × 500 mm<sup>2</sup> column.

mixture totalling 1–2 mequiv of Ti, Mo, and W, can be resolved with 27.5*M* hydrofluoric acid on a 203-mm column.

#### Separation of Ti, Mo, and W

The separation of Ti, Mo, and W with 27.5*M* hydrofluoric acid is shown in Fig. 4. A 210-mm column was used for the sample containing 100 mg of each of these elements and 700 mg of Nb in 30 ml of 3*M* hydrofluoric acid, the calculated column length being increased by 7 mm which is about half the length of column occupied by the initial load, assuming 100% loading efficiency. Column loading was ~7%. Although quantitative separations were achieved, the elution curves were separated by 25 ml or less. For practical application, when a greater interval between elution curves might be desired, a column length of 240 mm or more would be better, but smaller amounts of these elements are adequately separated on a 210-mm column. The elution curve of W (Fig. 4) tails somewhat. More efficient removal of this element can be accomplished with, *e.g.*, 7*M* hydrochloric–3*M* hydrofluoric acid mixture.<sup>7</sup>

#### Separation of V, Ti, Mo and W

*Calculation of the column length.* It has been shown that V can be separated with 10.1*M* hydrofluoric acid, and Ti (or Zr), Mo and W with 27.5*M* hydrofluoric acid. It should be possible to resolve a mixture of all these elements by combining the two systems.

To calculate the required column length the displacement of the other elements during removal of V with 10.1*M* hydrofluoric acid must be evaluated. According to Faris, the distribution coefficients of Ti and Mo in 10.1*M* hydrofluoric acid are about the same and that of W is higher, so Ti and Mo should be equally displaced by a given volume of 10.1*M* hydrofluoric acid, and W should be displaced

less. Since the 27.5M acid elutes Mo before W, this difference in displacement would enhance their subsequent separation. Accordingly, evaluation based on the elution behaviour of Mo should be adequate.

The displacement  $d$  mm of a solute on a column by passage of a volume  $U$  of eluent is given by the equation.

$$d = \frac{UH}{C V_1} \quad (5)$$

For a column with 25 mm diameter, such as was used in this work, the column volume is approximately 0.5H ml if  $H$  is in mm. Since the interstitial volume has been determined to be 46% of the column volume,  $V_1 \approx 0.23H$ . Substitution into equation (5) yields

$$d = \frac{U}{0.23C} \quad (6)$$

If we let  $U$  equal  $U_V^*$ , the volume of 10.1M hydrofluoric acid required to move the peak of the V band to the bottom of the column, and substitute 0.23H for  $V_1$  in equation (1) to obtain  $U_V^*$  in terms of  $H$  and  $C_V$ , then the displacement of Mo, up to the point where maximum elution of V occurs, becomes

$$d = \frac{C_V H + H}{C_{Mo}} \quad (7)$$

However, the complete removal of V requires an additional volume of 10.1M hydrofluoric acid, resulting in further displacement of Mo, calculable from equation (5) if the volume of eluent is known. The extra eluent required to bring the removal of V to 99.95% can be calculated by

$$U = 3.29 U_V^* \sqrt{\frac{C_V}{P_V H (C_V + 1)}} \quad (8)$$

where the value 3.29 has the same significance as in equation (4). Combination of equations (1) and (8) and substitution of 0.23H for  $V_1$  yields

$$U = 0.76 \sqrt{\frac{H(C_V^2 + C_V)}{P_V}} \quad (9)$$

Combining this with equation (6) gives

$$d = \frac{3.3}{C_{Mo}} \sqrt{\frac{H(C_V^2 + C_V)}{P_V}} \quad (10)$$

Thus the total displacement of Mo is the sum of equations (7) and (10). The values for  $C_V$  and  $P_V$  were taken as the average of those determined for 8.7 and 11.6M hydrofluoric acid. The value of  $C_{Mo}$  was determined separately to be 37. The displacement of Mo was calculated to be  $0.3H + 1.9\sqrt{H}$ . Since a column length of at least 210 mm is required for the separation of Ti, Mo and W with 27.5M hydrofluoric acid (Fig. 4), for the separation of V, Ti, Mo and W at least 210 mm of column must be available beyond the Mo band after the elution of V with 10.1M hydrofluoric acid, i.e.,  $0.3H + 1.9\sqrt{H} + 210 = 350$  mm.

By means of equations (1) and (9) it was determined that the elution of V from such a column would require 1200 ml of eluent, and at a flow-rate of 2.5 ml/min the removal of V would take 8 hr.

*Application of coupled columns.* It has been shown that coupled columns can be used in place of a single long column to improve the efficiency of separation of multicomponent mixtures,<sup>1</sup> a considerable reduction in time and eluent volume being realized. The time required for the separation of V is reduced by over 4 hr by use of this technique.

In the original method, 13M hydrofluoric acid was used to elute V from a 200-mm column, but with 10.1M hydrofluoric acid as eluent the first section need be only 125 mm long (Fig. 2). The displacement of Mo on this 125-mm column would be 59 mm. Adding 7 mm to allow for half the height of the original load band (assuming 100% loading efficiency and an 11-mequiv load), the estimated position of the Mo band becomes 66 mm from the top of the first section, leaving ~60 mm of this section available for subsequent separations. Since 240 mm are required, the second section should be 180 mm long.

The technique was tested on a sample containing 100 mg each of V, Ti, Mo and W and 600 mg of Nb in 30 ml of 3M hydrofluoric acid, transferred to a 125-mm column pretreated with the 3M acid. The V was eluted with 10.1M hydrofluoric acid, its removal being complete at an eluate volume of 525 ml. A 180-mm column pretreated with 27.5M hydrofluoric acid was attached to the bottom of the first column by means of polyethylene tubing fitted in a neoprene stopper which was inserted into the top of the second section. Then the 27.5M acid was passed through until the Ti and Mo had been eluted. The sections were then separated and W was eluted from the lower section with 7M

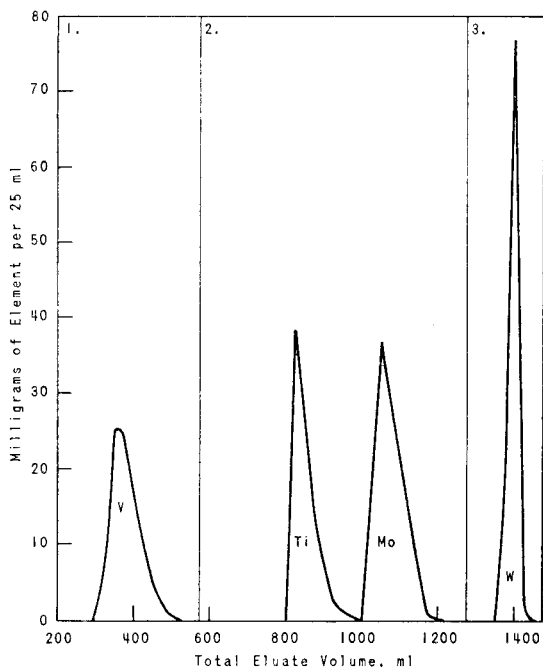


FIG. 5.—Separation of vanadium, titanium, molybdenum and tungsten.

- 1—Elution of V with 10.1M HF through a 125-mm column.
- 2—Elution of Ti and Mo with 27.5M HF through coupled 125-mm and 180-mm columns.
- 3—Elution of W with 7M HCl–3M HF through lower 180-mm column.

hydrochloric–3M hydrofluoric acid. The Nb was eluted from the upper section with 3M ammonium chloride–1M hydrofluoric acid.<sup>7</sup> All the Nb had been retained in the upper section while all of the W had passed into the lower section. Photometric analyses of all of the fractions except those containing Nb from the upper section, produced the elution curves shown in Fig. 5.

Figure 5 shows that quantitative separations were achieved, although there was no latitude in the separation of Ti and Mo. Separation could be improved by increasing the length of the second section, but 50-mg amounts of these elements are adequately separated with a 180-mm second section.

#### Separation schemes

On the basis of these elution and separation studies, separation schemes were devised for various combinations of Nb and two or more of the other elements studied. All but one of the possible mixtures can be resolved by using the appropriate scheme from those shown in Table V. Relatively large amounts of Nb are assumed present and can be eluted last with 3M ammonium chloride–1M hydrofluoric acid.

The separation of Ti, Mo and W by Scheme C was shown in Fig. 4 and the application of coupled columns, Scheme D, to the separation of V, Ti, Mo and W was shown in Fig. 5. It was mentioned earlier that although their elution curves do not overlap, a greater interval between Ti and Mo and between Mo and W would be desirable. In each case 100-mg amounts of the elements were taken. Separations more suitable for practical application should be achieved with smaller amounts without increasing the column lengths. The separations listed in Table V were therefore tested experimentally on mixtures containing 70 mg each of the appropriate elements and approximately 900 mg of Nb, dissolved in 30 ml of 3M hydrofluoric acid. Fractions were collected and tested semi-quantitatively to follow the elution of each element.

In the separation of Zr and Ti, W and Nb and of V, W and Nb by Scheme A the elution curves are separated by intervals convenient for practical application. In Scheme B the elution of Zr and Ti could be accomplished with 3M hydrochloric–5.8M hydrofluoric acid mixture as well as the 7M hydrochloric–3M hydrofluoric acid mixture.<sup>8</sup>

TABLE V.—SEPARATION SCHEMES

Scheme	Column length, <i>mm</i>	Eluents	Elements eluted
A	110	27·5 <i>M</i> HF (300 ml) 7 <i>M</i> HCl–3 <i>M</i> HF (175 ml)	V, Zr or Ti W
B	125	10·1 <i>M</i> HF (525 ml) 7 <i>M</i> HCl–3 <i>M</i> HF (300 ml)	V Zr or Ti
C	210	27·5 <i>M</i> HF (650 ml) 7 <i>M</i> HCl–3 <i>M</i> HF (200 ml)	V, Zr or Ti in first fraction Mo in second fraction W
D	125-mm section 125-mm + 180-mm sections 180-mm section	10·1 <i>M</i> HF (525 ml) 27·5 <i>M</i> HF (750 ml) 7 <i>M</i> HCl–3 <i>M</i> HF (200 ml)	V Zr or Ti in first fraction Mo in second fraction W

Separations by Scheme C were satisfactory, with ~50-ml intervals between successive elements, except for a mixture of Zr, Ti, Mo, W and Nb, where Ti and Mo were separated by only ~25 ml.

According to Table V, Scheme C uses a 210-mm column and 27·5*M* hydrofluoric acid followed by 7*M* hydrochloric–3*M* hydrofluoric acid as eluents. The latter is used to elute W if it is present, but can be left out if W is absent. In each of the separations tested, Mo was eluted with the 27·5*M* acid. When W is absent, Mo can be eluted with 3*M* hydrochloric acid–5·8*M* hydrofluoric acid if desired, to minimize the use of the 27·5*M* acid. The 7*M* hydrochloric–3*M* hydrofluoric acid mixture is not a suitable eluent for Mo.<sup>8</sup>

It was calculated earlier that the separation of small amounts of Ti and Mo with 27·5*M* hydrofluoric acid could be accomplished with a 132-mm column. However, in view of the proximity of the elution curves of Ti and Mo in Figs. 4 and 5, a column shorter than 210 mm could not be expected to provide enough latitude in the separation of these two elements. The same would apply to the separation of V and Mo (see Fig. 3). An interval of 50 ml was realized in each case by use of a 210-mm column.

The separations with coupled columns (Scheme D) gave a latitude of 25 ml between Ti and Mo which is better than that in Fig. 5. Unless a greater interval is desired, the length of the second section need not be increased for handling < 70 mg.

For the separation of V, Zr and Ti, Mo and Nb, elution through the coupled columns with 27·5*M* hydrofluoric acid was continued until Mo began to elute. At this point, the sections were disconnected and the remainder of the Mo in the lower 180-mm section was eluted with the same eluent, while Nb was removed from the 125-mm section as usual.

The one combination for which a separation scheme is not taken from Table V is that of V, Zr and/or Ti, W, and Nb. This mixture can be readily resolved by means of a single 125-mm column, eluting V with 10·1*M* hydrofluoric acid, as in Scheme B, then Zr and/or Ti with 27·5*M* acid and finally W and Nb in that order with the usual eluents.<sup>7</sup>

## DISCUSSION

From a practical standpoint it must be remembered that variations in flow-rate, column length and particle size will affect the ion-exchange behaviour of the elements. Differences may be observed with different lots of the same resin. However, in applying the schemes developed here to analytical problems, given the same type of resin it should be possible to duplicate the separations, provided the same experimental conditions are maintained.

For routine applications, wider intervals between successive solutes may be desired to allow for differences in the relative amounts of solutes to be separated and for such incidental differences as may occur in flow-rate and sample and washing volumes. With this in mind, simplified equations were derived which allow the calculation of the column length needed to provide any desired theoretical interval in the separation of V and Zr, Ti and Mo, and Mo and W with the appropriate eluents, since these are the critical separations.

The separation of two solutes is dependent on the positions of the trailing edge of the solute which elutes first and the leading edge of the next solute. The elution of the first solute is complete at  $U_1^* + U_1$ , where  $U_1$  can be determined for the trailing edge of the first solute by means of equation (9), inserting the appropriate  $C$  and  $P$  values for the element under consideration. The elution of the next solute begins at  $U_2^* - U_2$ , where  $U_2$  is determined for the leading edge of the second solute. The interval between the solutes, then, is  $(U_2^* - U_2) - (U_1^* + U_1)$ .

It has been shown that the interstitial volume  $V_i$  is 46% of the column volume and is equal to  $0.23H$  for a column 25 mm in diameter. Substituting this in equation (1) it can be shown that  $U_2^* - U_1^* = 0.23H(C_2 - C_1)$ . The interval then becomes  $0.23H(C_2 - C_1) - U_2 - U_1$ . By means of the data listed in Tables III and IV, "interval" equations for the separations mentioned above have been obtained in which the interval is expressed as a function of column length. These are shown in Table VI.

TABLE VI.—EQUATIONS DEFINING SEPARATION INTERVALS IN TERMS OF COLUMN HEIGHT

Elements separated	V and Zr	V and Zr	Ti and Mo	Mo and W
Eluent	8.7M HF	11.6M HF	27.5M HF	27.5M HF
Interval equation	$6.6H - 45.9\sqrt{H}$	$2.25H - 24.7\sqrt{H}$	$0.87H - 9.6\sqrt{H}$	$1.1H - 15.1\sqrt{H}$

According to the interval equation for the separation of Ti and Mo with 27.5M hydrofluoric acid, the column length calculated by equation (4) for this separation, 132 mm, would provide a theoretical interval of  $\sim 4$  ml. This is hardly adequate for practical application. If an interval of 100 ml is desired, the required column length can be determined by setting the interval equation equal to 100 and solving for  $H$ : e.g.,  $0.87H - 9.6\sqrt{H} = 100$ . The column height so determined is 310 mm. A 210-mm column would provide an interval of 44 ml. The interval actually obtained with 70-mg amounts was 50 ml.

It would be preferable, then, to determine the required column length on the basis of the desired interval rather than from equation (4). By modification of equation (4) to provide a higher degree of purity, the calculated column length is, of course, larger. It was pointed out earlier that use of the value 3.74 instead of 3.29 provides for a purity of 99.99%. For the separation of Ti and Mo the calculated column length becomes 170 mm. According to the interval equation this length would provide a separation interval of 23 ml. Thus, where an interval of 50 ml is desired, equation (4) does not provide an adequate column length with this higher criterion of purity.

The interval equation is also useful for determining how much the column length should be increased when overlapping occurs because of overloading. The column length determined from equation (4) for the separation of V and Zr with 8.7M hydrofluoric acid was 53 mm. The experimental elution curves obtained with a 60-mm column overlap by  $\sim 135$  ml. According to the interval equation for this separation a 60-mm column should separate these elements by 40 ml. The difference between the actual and theoretical intervals obtained with a 60-mm column is  $\sim 175$  ml. For a separation of 50 ml, the required column length should be obtained by setting the interval equation equal to  $175 + 50$  ml. The column height so determined is 105 mm.

This estimate, based on a single elution experiment with a 60-mm column, is quite impressive, in view of the experimental results obtained with a 90-mm column, where an overlap of only 50 ml was observed. This approach should prove useful for column separations in general where column loading is high and overlapping occurs.

In the separation of 100 mg amounts of Ti, Mo and W in the presence of 700 mg of Nb with a 210-mm column and 27.5M hydrofluoric acid, there was very little latitude between Ti and Mo and between Mo and W (Fig. 4). According to the interval equations, an improvement of 78 ml in the separation of Ti and Mo and of 49 ml between Mo and W would be achieved with a 270-mm column.

**Zusammenfassung**—Schemata für die Trennung zweier oder mehrerer von den Elementen Vanadium, Zirkonium und/oder Titan, Molybdän und Wolfram voneinander und von relativ großen Mengen Niob mit Hilfe eines stark basischen Anionenaustauscharzes wurden entwickelt. Durch die Verwendung von Flußsäure zur Elution von Vanadium, Zirkonium, Titan und Molybdän wird die Störung durch Niob vermieden. Um die Trennleistung in Vielkomponentengemischen zu verbessern, wird die Verwendung von gekoppelten Säulen demonstriert. Zur Berechnung der zu einem gegebenen Trennproblem notwendigen Säulenlänge wird eine "Intervall"-Gleichung vorgeschlagen, die das Volumenintervall zwischen zwei nacheinander eluierten Lösungskomponenten angibt. Diese Gleichung ist besonders nützlich, wenn berechnet werden soll, um welchen Betrag eine Säule verlängert werden muß, damit bei hoher Belastung der Säule auftretende Überlappung vermieden wird.

**Résumé**—On a élaboré des schémas pour la séparation de deux ou plusieurs des éléments: vanadium, zirconium et/ou titane, molybdène et tungstène l'un de l'autre et de quantités relativement importantes de niobium, en utilisant une résine échangeuse d'anions fortement basique. L'interférence du niobium est évitée en utilisant l'acide fluorhydrique pour éluer les vanadium, zirconium, titane et molybdène. On démontre que l'application de colonnes couplées améliore l'efficacité de séparation pour des mélanges à nombreux constituants. On propose l'emploi d'une équation d'"intervalle" définissant l'intervalle de volume entre solutés élués successivement pour calculer la longueur de colonne requise pour une séparation particulière. Cette équation est particulièrement utile pour déterminer jusqu'à quel une colonne doit être allongée lorsqu'un recouvrement se manifeste à cause d'une forte charge de colonne.

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## REACTION OF GALLIUM AND INDIUM WITH 4-(2-THIAZOLYLAZO) RESORCINOL

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**Summary**—Gallium is shown to react with TAR to form 1:1 and 1:2 Ga:TAR species, elucidation of the nature of which is complicated by hydrolysis. The species  $\text{GaR}^+$  and  $\text{GaHR}(\text{OH})^+$ , where  $\text{H}_2\text{R}$  is the free reagent, occur at pH 2.7–4.8 for solutions that are equimolar or contain excess of metal ion;  $\text{GaHR}^{2+}$  occurs at pH 2.13–2.86 with excess of metal ion. A 1:2 complex, probably  $\text{GaR}_2^-$ , exists in 30% aqueous ethanol medium at pH  $\sim 5$  if excess of ligand is present. The utility of the reaction for analysis is severely limited by the large number of interfering elements. Indium reacts similarly, forming a  $\text{InRH}^{2+}$  complex which is converted into the 1:2 complex by excess of reagent at pH 4.6.

AZO-DIHYDROXY dyes, especially those derived from pyridine, are sensitive chromogenic reagents for gallium and indium. 1-(2-Pyridylazo)-2-naphthol<sup>1–3</sup> and 4-(2-pyridylazo)resorcinol (PAR)<sup>4–9</sup> have both been used despite the fact that various complexes ( $\text{MHR}^{2+}$ ,  $\text{MR}^+$  and  $\text{MR}_2^-$ , where  $\text{H}_2\text{R}$  is the reagent) may be formed under very similar conditions. This paper describes the reaction of gallium and indium with the thiazolyl analogue of PAR<sup>3</sup> 4-(2-thiazolylazo) resorcinol (TAR).

### EXPERIMENTAL

#### Reagents

**Gallium perchlorate solution.** "Specpure" gallium oxide (Johnson and Matthey) was fused with potassium pyrosulphate, and the cooled melt dissolved in dilute sulphuric acid. Gallium hydroxide was precipitated by addition of ammonia, separated, and dissolved in perchloric acid (1 + 1). The solution was diluted to about 1*N* acidity and standardized gravimetrically *via* gallium oxide.

**Indium perchlorate solution.** "Specpure" indium oxide (Johnson and Matthey) was treated by repeated addition and evaporation of 35% v/v perchloric acid, being finally dissolved in 2*M* perchloric acid and standardized gravimetrically.

**TAR solutions.** A purified sample was twice recrystallized from hot ethanol, and its purity checked by elemental analysis, water and ash determination, titration with chromium(II) chloride<sup>10</sup> and descending chromatography with butanol-acetic acid-water (2:1:1). Solutions were prepared in sodium hydroxide, pH 11–12, or in ethanol.

**Buffers.** The pH was generally adjusted with perchloric acid, ammonia and sodium hydroxide. Buffers were used only in the practical procedures, and were 1*M* acetic acid adjusted to pH 4.2, 4.6 or 5.0 with sodium hydroxide, or were 0.5*M* pyridine adjusted to pH 4.2, 5.0 or 5.5 with perchloric acid. The ionic strength was kept constant at 0.1 by addition of sodium perchlorate. The pH values for 30% v/v ethanol solutions are uncorrected.

#### Physical constants for TAR

The following values were used.<sup>11</sup>

$$pK_{a1}(\text{NH}^+) 0.98; pK_{a2}(p\text{-OH}) 6.23; pK_{a3}(o\text{-OH}) 9.44$$

	$\epsilon_{\text{H}_2\text{R}^+}$	$\epsilon_{\text{H}_2\text{R}}$	$\epsilon_{\text{RH}^-}$	$\epsilon_{\text{R}^{2-}}$
500 nm	$2.90 \times 10^4$	$3.46 \times 10^3$	$2.04 \times 10^4$	$3.31 \times 10^4$
530 nm	$1.18 \times 10^4$	$3.40 \times 10^3$	$6.01 \times 10^3$	$3.07 \times 10^4$



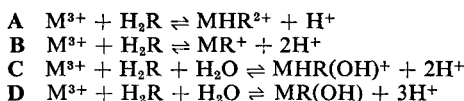
### Absorption spectra

Figures 1 and 2 show the absorption spectra for solutions containing an excess of gallium and for equimolar solutions. At  $\text{pH} < 4.5$ ,  $\lambda_{\text{max}}$  is 500–505 nm, with an isosbestic point at 455 nm which is clear evidence of formation of a single complex under these conditions. For solutions with a small excess of reagent and at  $\text{pH} 5.4$  a correction must be made for the absorbance of the free ligand, and  $\lambda_{\text{max}}$  is 510–515 or 505–510 nm, depending on whether a 1:1 or a 1:2 complex is assumed present.

Figures 3 and 4 show the spectra for indium. With excess of metal ion at  $\text{pH} 1.6$ – $3.5$ ,  $\lambda_{\text{max}}$  occurs at 530–535 nm, but there is no sharp isosbestic point because both  $\text{H}_3\text{R}^+$  and  $\text{H}_2\text{R}$  react simultaneously. Two equilibria may be distinguished on the curves for equimolar solutions, one complex being formed at  $\text{pH} 2.76$ – $3.82$  ( $\lambda_{\text{max}}$  530 nm) and the other at  $\text{pH} 4.29$ – $5.85$  ( $\lambda_{\text{max}}$  505 nm). The curves with excess of TAR present are similar to the gallium ones.

### Absorbance–pH plots

In equimolar solutions the gallium complex is formed at  $\text{pH} > 2.8$ , and in solutions with excess of metal ion, even at  $\text{pH} < 2$  (Fig. 5, curves 1–5), formation occurring at lower pH with increasing concentration of metal ion or ligand. The corresponding indium curves are in Fig. 6. Only the first upward slopes of the curves were interpreted, by the slope–intercept transformations given earlier.<sup>12–16</sup> By analogy with other TAR systems the equilibria were assumed to be accompanied by the following basic equations.



### Solutions with metal ion excess

$$C_M \sim [\text{M}]; \quad C_R = [\text{complex}] + [\text{H}_2\text{R}] + [\text{H}_3\text{R}^+]; \quad A = \epsilon_1 [\text{complex}] + \epsilon_{R1}[\text{H}_3\text{R}^+] + \epsilon_{R2}[\text{H}_2\text{R}]$$

$$\frac{C_R}{A} = \frac{1}{\epsilon_1} + \frac{a[\text{H}^+]^x}{AC_M k_1 \epsilon_1} \quad (1)$$

$$\log \frac{a}{\epsilon_1 C_R - A} = x\text{pH} + \log C_M + \log k_1 \quad (2)$$

$$a = A \left( 1 + \frac{[\text{H}^+]}{K_{a1}} \right) - C_R \left( \epsilon_{R1} \frac{[\text{H}^+]}{K_{a1}} + \epsilon_{R2} \right)$$

where it is assumed that  $\text{H}_2\text{R}$  is the reacting species;  $C_M$  and  $C_R$  are the analytical concentrations of metal and reagent;  $\epsilon_1$ ,  $\epsilon_{R1}$  and  $\epsilon_{R2}$  are the molar absorptivities of the complex,  $\text{H}_3\text{R}^+$  and  $\text{H}_2\text{R}$  respectively;  $k_1$  is the formation constant of the 1:1 complex;  $A$  is the absorbance;  $x$  is 1 for **A**, 2 for **B** and **C**, 3 for **D**.

### Equimolar solutions ( $C_M = C_R$ )

$$C_R = [\text{complex}] + [\text{H}_2\text{R}]; \quad C_M = [\text{complex}] + [\text{M}]; \quad A = \epsilon_1 [\text{complex}] + \epsilon_{R2}[\text{H}_2\text{R}]$$

$$\frac{C_R}{A} = \frac{1}{\epsilon_1} + \frac{\sqrt{[\text{H}^+](A - \epsilon_{R2}C_R)}}{A} \cdot \frac{1}{\epsilon_1} \sqrt{\frac{\epsilon_1 - \epsilon_{R2}}{k_1}} \quad (3)$$

$$\log \frac{A - \epsilon_{R2}C_R}{(\epsilon_1 C_R - A)^2} = x\text{pH} - \log(\epsilon_1 - \epsilon_{R2}) + \log k_1 \quad (4)$$

The symbols have the same significance as before, and  $\text{H}_3\text{R}^+$  is ignored under the conditions given.

Plots such as  $C_R/A = f([\text{H}^+])$  do not give an exactly straight line for any of the gallium equilibria considered, indicating overlapping equilibria for these conditions ( $C_M = 7.62 \times 10^{-4}$ – $4.7 \times 10^{-3}M$ , or  $C_M/C_R = 19$ – $122$ ,  $\text{pH} 2.7$ – $4.8$ ), but since 2 protons are liberated in formation of one complex molecule, evidently equilibria **B** and **C** are involved in formation of a 1:1 complex, but they cannot be distinguished by photometric analysis. At  $\text{pH} 2.13$ – $2.86$  and  $C_M = 9.36 \times 10^{-3}M$ ,  $C_M/C_R = 245$ , equilibrium **A** is the only one existing.

For indium at  $\text{pH} > 1.6$  equilibrium **A** is operative, but at  $\text{pH} > 3.5$  and with metal ion in excess ( $C_M = 1.23$ – $9.55 \times 10^{-4}M$ ) equilibrium **B** appears to predominate, but curve analysis was not possible, owing to hydrolysis effects.

The apparent molar absorptivity values extrapolated from graphical plots [equations (1) and (3)] were identical for solutions with excesses of gallium, but different from that for  $C_M = C_R = 3.62 \times$

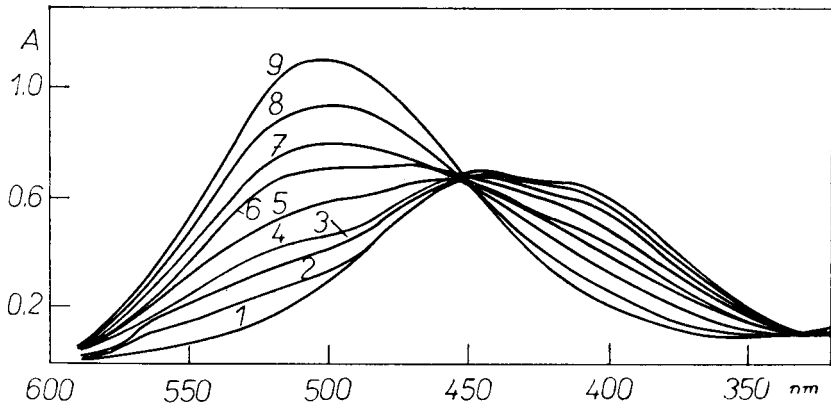


FIG. 1.—Absorption spectra for TAR-solutions with excess of Ga<sup>3+</sup>.

$C_R = 3.82 \times 10^{-5}M$ ;  $C_M = 1.78 \times 10^{-3}M$ ; pH: 1—1.68; 2—2.07; 3—2.24; 4—2.34; 5—2.49; 6—2.61; 7—2.72; 8—2.89; 9—3.13.

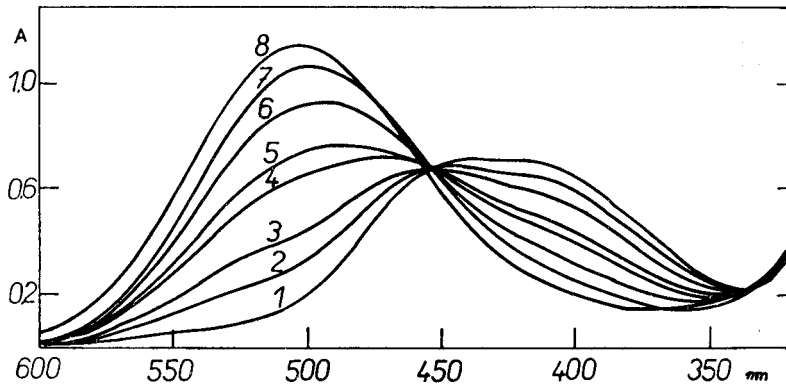


FIG. 2.—Absorption spectra for equimolar solutions of TAR and Ga<sup>3+</sup>.

$C_M = C_R = 3.62 \times 10^{-5}M$ ; pH: 1—2.81; 2—3.25; 3—3.43; 4—3.68; 5—3.76; 6—4.02; 7—4.33; 8—5.83.

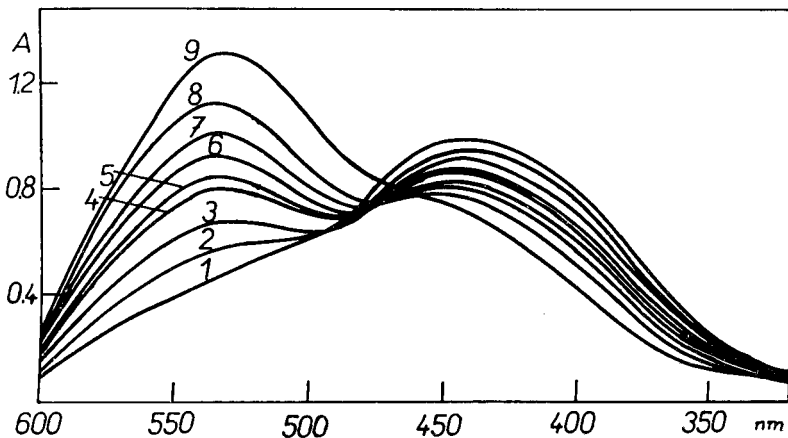


FIG. 3.—Absorption curves for TAR solutions with excess of In<sup>3+</sup>.

$C_R = 5.64 \times 10^{-5}M$ ;  $C_M = 2.86 \times 10^{-3}M$ ; pH: 1—1.65; 2—1.81; 3—1.94; 4—2.10; 5—2.17; 6—2.29; 7—2.68; 8—2.95; 9—3.48.

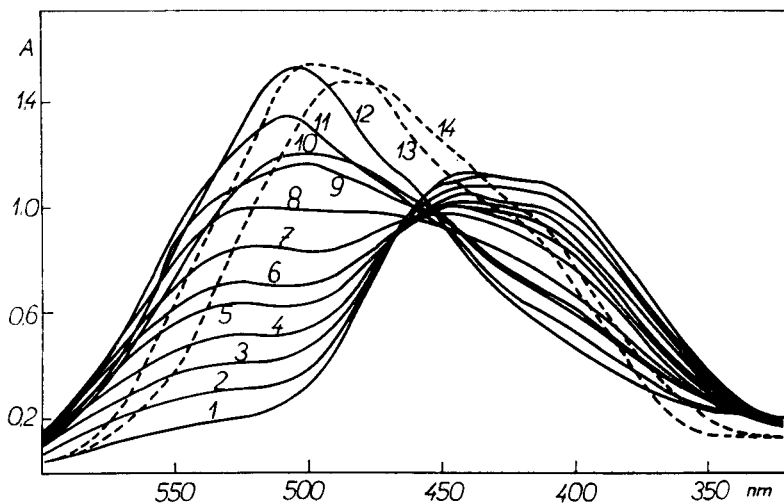


FIG. 4.—Absorption curves for equimolar solutions of TAR with  $\text{In}^{3+}$ .  
 $C_M = C_R = 5.97 \times 10^{-5} M$ ; pH: 1—2.76; 2—3.08; 3—3.30; 4—3.50; 5—3.70;  
 6—3.82; 7—4.00; 8—4.29; 9—4.73; 10—5.33; 11—4.75; 12—5.85; 13—8.51;  
 14—9.38.

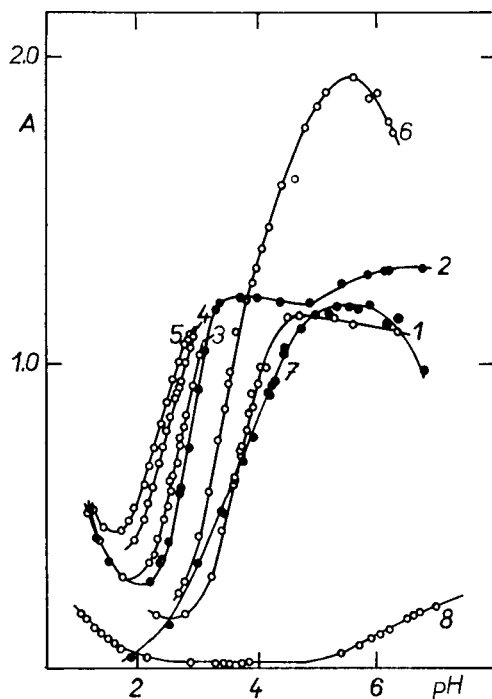


FIG. 5.—Absorbance-pH plots for TAR and  $\text{Ga}^{3+}$  solutions.  
 $\lambda = 500 \text{ nm}$ ; 1— $C_R = C_M = 3.62 \times 10^{-5} M$ ; 2— $C_R = 3.99 \times 10^{-5} M$ ,  $C_M/C_R = 19.1$ ;  
 3— $C_R = 3.82 \times 10^{-5} M$ ,  $C_M/C_R = 46.7$ ; 4— $C_R = 3.84 \times 10^{-5} M$ ,  $C_M/C_R = 122$ ;  
 5— $C_R = 3.82 \times 10^{-5} M$ ,  $C_M/C_R = 245$ ; 6— $C_M = 3.62 \times 10^{-5} M$ ,  $C_R/C_M = 3$ ;  
 7— $C_M = 1.91 \times 10^{-5} M$ ,  $C_R/C_M = 30.3$ ; 8— $C_R = 3.82 \times 10^{-5} M$ .

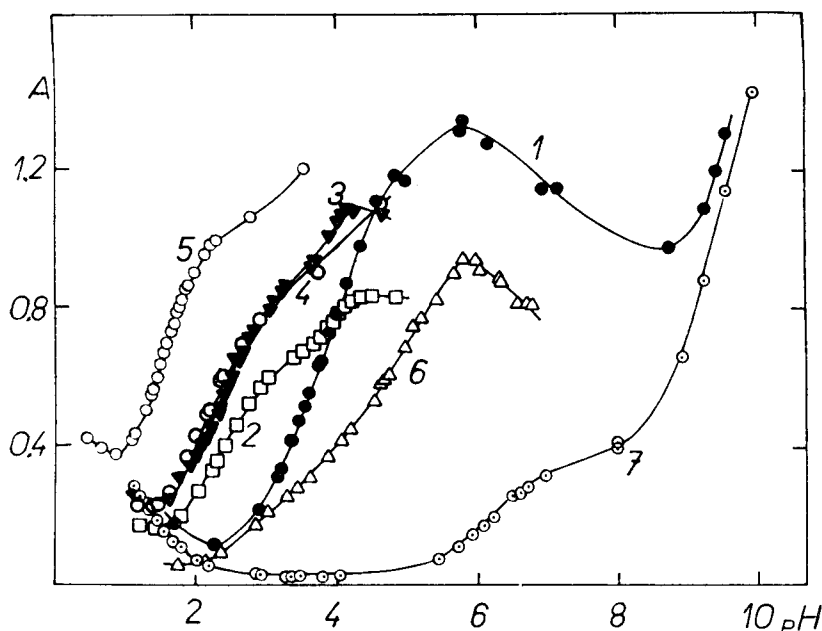


FIG. 6.—Absorbance-pH plots for the TAR-indium system at 530 nm.

1— $C_M = C_R = 5.97 \times 10^{-5} M$ ; 2— $C_M = 1.23 \times 10^{-5} M$ ,  $C_M/C_R = 40.1$ ; 3— $C_M = 1.23 \times 10^{-5} M$ ,  $C_M/C_R = 30.2$ ; 4— $C_M = 1.91 \times 10^{-5} M$ ,  $C_M/C_R = 50.0$ ; 5— $C_M = 9.55 \times 10^{-5} M$ ,  $C_M/C_R = 199$ ; 6— $C_M = 2.26 \times 10^{-5} M$ ,  $C_R/C_M = 20.0$ ; 7— $C_R = 5.97 \times 10^{-5} M$ ,  $C_M = 0$ .

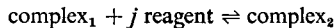
$10^{-5} M$ . If these values were inserted in equations (2) and (4), better values for  $x$  were obtained as well as particular equilibrium constants. These logarithmic plots confirmed that 1 or 2 protons were liberated per complex molecule formed, in the pH interval examined.

The apparent molar absorptivities for the 1:1 complexes were  $3.2\text{--}3.9 \times 10^4$  at 500 nm and  $2.7\text{--}2.8 \times 10^4$  at 530 nm for  $C_{Ga}/C_{TAR}$  ratios 0.33–245 and pH 2.1–4.0, and  $2.24\text{--}2.50 \times 10^4$  at 530 nm for  $C_{In}/C_{TAR}$  ratios 1–199 and pH 1.9–2.6.

#### Absorbance-[ligand] plots for 30% v/v ethanol solutions

In these plots no horizontal part was reached for gallium at any pH between 4.35 and 5.25 and  $\lambda = 530$  nm, so no one gallium-TAR complex was formed exclusively and quantitatively even with a 40-fold excess of ligand. The limiting values of the apparent molar absorptivity depended markedly on pH. Corrections were applied for the absorbance of the excess of ligand. Similar results were obtained for indium at pH 4.15–6.07.

The curves were examined for evidence of stepwise complex formation, by means of the following equations<sup>12</sup>.



$$C_M = [\text{complex}_1] + [\text{complex}_2]; \quad C_R \sim [H_2R] + [HR^-]$$

$$\Delta A = \epsilon_1[\text{complex}_1] + \epsilon_2[\text{complex}_2]$$

$$\Delta A = \epsilon_1 C_M + (\epsilon_2 C_M - \Delta A) C_R^j / \text{constant} \quad (5)$$

$$\Delta A = \epsilon_2 C_M - (\Delta A - \epsilon_1 C_M) \text{constant} / C_R^j \quad (6)$$

The quantities  $A_{01} = \epsilon_1 C_M$  and  $A_{02} = \epsilon_2 C_M$  were successively approximated, assuming  $j = 1$  or 2 (formation of complexes higher than 1:3 was not supposed). The plot of the function  $\Delta A = f(\Delta A/C_R^j)$  was not linear for either  $j = 1$  or  $j = 2$ . The limiting values  $\Delta A_{1im}$  of this plot and at least two other values of  $\Delta A_{02}$  were inserted in equation (5). The intercept obtained on plotting these values in

equation (5) established that two complexes co-existed over a wide concentration range. The approximate value of  $A_{01}$  from equation (5) was inserted in equation (6) and the successive approximation of  $A_{01}$  and  $A_{02}$  repeated there. The most precise values obtained were then inserted in

$$\log \frac{\Delta A - \varepsilon_1 C_M}{\varepsilon_2 C_M - \Delta A} = j \log C_R + \text{constant} \quad (7)$$

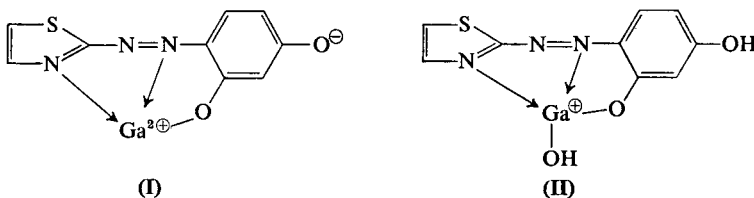
to establish the number of ligands in the complex. This graphical analysis showed that the 1:1 gallium complex is converted into the 1:2 complex at  $\text{pH} > 4.18$  in solutions with  $C_M = 1.12 \times 10^{-5} M$  and  $C_M = 3.3\text{--}63.0 \times 10^{-5} M$  i.e.,  $j = 1$ . The values  $\varepsilon_1 = 2.3 \times 10^4$  and  $\varepsilon_2 = 6.25 \times 10^4$  at 530 nm were calculated from the limits of plots of equations (5) and (6); this  $\varepsilon_1$  is lower than that calculated from results with equimolar solutions or those with metal ion excess. At  $\text{pH} 4.94$  almost the same value of  $\varepsilon_2$  is obtained from an  $A$  vs. [ligand] plot, but the curve analysis is complicated by simultaneous hydrolysis of the chelates or of free gallium. The absorbance increases slowly with time but is nearly constant if there is more than a 25-fold molar excess of ligand.

Job plots (at 500–540 nm) indicate a mixture of 1:1 and 1:2 gallium complexes at  $\text{pH} 3.3\text{--}5.4$  with the 1:1 complex predominating.

The 1:1 indium complex is converted into the 1:2 complex at  $\text{pH} 4.60$  in solutions with  $C_M = 1.34 \times 10^{-5} M$  and  $C_R > 10^{-4} M$ . The molar absorptivities are  $\varepsilon_1 = 2.24 \times 10^4$  and  $\varepsilon_2 = 5.22 \times 10^4$  at 530 nm, the first being in agreement with the value for the  $\text{InHR}^{2+}$  complex. At  $\text{pH} 5.3$  it is more probable that the 1:2 complex is formed directly from its components than by stepwise formation, if  $C_R$  is  $> 10^{-4} M$ . The structures of this complex cannot be decided by curve analysis but the small increase in  $\varepsilon_2$  with  $\text{pH}$  makes it likely that both  $\text{In}(\text{HR})_2^+$  and  $\text{InR}_2^-$  are present. Job curves for equimolar solutions indicate a 1:1 complex at  $\text{pH} < 4.4$  and a 1:2 complex at  $\text{pH} 5.20$  in 30% v/v ethanol.

## RESULTS

The complex  $\text{GaHR}^{2+}$  is formed at  $\text{pH} > 2.5$  in presence of excess of metal ion, and another 1:1 complex is formed at  $\text{pH} < 4$  in solutions that are equimolar or have metal ion excess, but curve analysis cannot distinguish between equilibria **B** and **C**.



However, for formation of a Ga-complex such as **I** at  $\text{pH} < 4$  it must be assumed that the *p*-hydroxy group in  $\text{GaRH}^{2+}$  must be more acidic than is indicated by  $\text{p}K_{a2}$  (6.23) and this must be attributed to an inductive effect similar to that observed earlier for particularly stable MRH complexes of PAR and TAR<sup>11,17</sup> or in solutions containing excess of highly charged metal ion. In comparison with other TAR complexes<sup>16</sup> the molar absorptivity of  $\text{GaRH}^{2+}$  ( $3.5 \times 10^4$  at 500 nm and  $2.8 \times 10^4$  at 530 nm) is anomalously high. Moreover, in contrast to other PAR and TAR complexes, the molar absorptivity of the 1:1 gallium-TAR complex does not change much in conditions which should lead to conversion of MRH into MR. Hence the liberation of  $\sim 2$  protons per complex molecule in equimolar solutions at  $\text{pH} < 4.0$ , and the tendency of gallium(III) to hydrolyse<sup>18</sup> make probable equilibrium **C** and structure **II**. Constants for 1:1 complexes are collected in Table I.

A 1:2 Ga-TAR complex, probably  $\text{GaR}_2^-$ , exists in 30% v/v aqueous ethanol containing a limited excess of ligand, but the equilibria cannot be delineated in detail, because of hydrolysis.

The  $\text{InRH}^{2+}$  is predominantly formed at  $\text{pH} > 1.6$  in solutions with TAR-excess. It is converted to  $\text{InRH}^+$  at  $\text{pH} > 3.0$  but hydrolysis equilibria interfere for the curves

TABLE I.—EQUILIBRIUM CONSTANTS FOR 1:1 COMPLEXES

	Gallium	Indium
$k_{11H} = [\text{MRH}][\text{H}]/[\text{M}][\text{H}_2\text{R}]$	$\log k_{11H} = -0.33^*$	0.62; 0.61
$k_{12H} = [\text{MRH}][\text{H}]^2/[\text{M}][\text{H}_3\text{R}]$	$\log k_{12H} = -1.32$	-0.36
$k_{12} = [\text{MR}][\text{H}]^2/[\text{M}][\text{H}_2\text{R}]$	$\log k_{12} = -2.83^\dagger; -2.70^\ddagger$	
$K_{1H} = [\text{MRH}]/[\text{M}][\text{HR}^*]^\S$	$\log K_{1H} = 9.1$	10.06
$K_1 = [\text{MR}]/[\text{M}][\text{R}]$	$\log K_1 = 12.8$	

$\log k_{11H} = -\text{pH} - \log C_M$ ;  $\log k_{12H} = -2\text{pH} - \log C_M$ ;  $\log k_{12} = -2\text{pH} + \log(\epsilon_1 - \epsilon_R)$ ;  
 $k_{12H} = k_{11H} \cdot K_{a1}$ ;  $K_{1H} = k_{11H}/K_{a3} = k_{12H}/K_{a1} \cdot K_{a3}$ ;  $K_1 = k_{12}/K_{a2} \cdot K_{a3}$ .

\* For metal ion excess and pH 2.13 - 2.70.

† For equimolar solutions and pH < 4.0, equation (4).

‡ Equation (3).

§ For meaning of HR\*, see Ref. 15.

interpretation. Both,  $\text{In}(\text{RH})_2^+$  and  $\text{InRH}_2^-$  complexes exist in solutions with ligand excess ( $C_R > 10^{-4}M$ ) from pH 4.6 but the sole formation of 1:2-complex is only evident from pH 5.3.

### Spectrophotometric determination of gallium and indium

It is difficult to find conditions for the existence of a single gallium or indium TAR species in the presence of excess of ligand, so any methods of determination based on the TAR system must be based on fairly close control of reaction conditions. Hence the apparent molar absorptivity is strongly dependent on pH and reagent concentration in solutions containing 30% v/v ethanol (Figs. 7 and 8). If the excess of reagent is >20-fold ( $C_R > 3.5 \times 10^{-4}M$ ) the absorbance for a fixed gallium or indium concentration is almost independent of pH over the narrow range 5.0-5.7, for gallium or pH 5.3-6.0 for indium, but even so, the apparent molar absorptivity difficulty reaches the theoretical for the  $\text{MR}_2^-$ -chelate ( $\epsilon_2 = 6.25 \times 10^4$  at 530 nm) at the

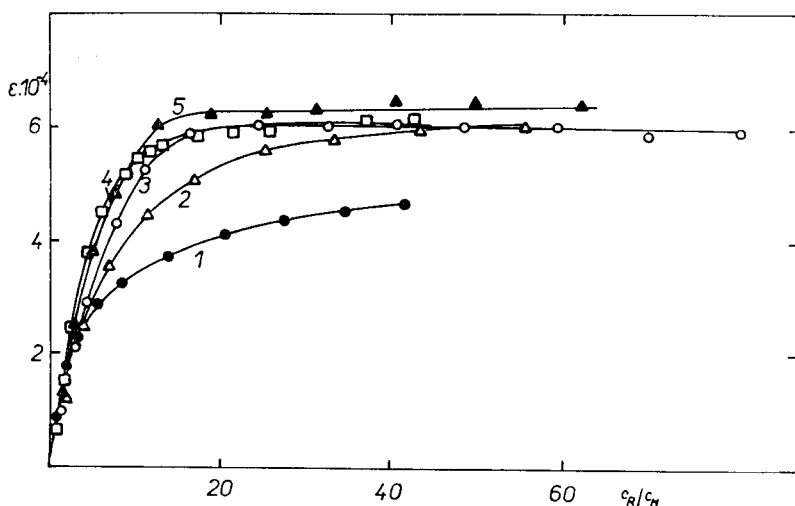


FIG. 7.—Plot of apparent molar absorptivity vs.  $C_R$  in 30% v/v ethanol at 525 nm, for gallium.

1—pH 4.15;  $C_M = 1.63 \times 10^{-5}M$

2—pH 4.59;  $C_M = 1.30 \times 10^{-5}M$

3—pH 4.04;  $C_M = 1.17 \times 10^{-5}M$

4—pH 5.30;  $C_M = 1.78 \times 10^{-5}M$

5—pH 5.70;  $C_M = 1.02 \times 10^{-5}M$

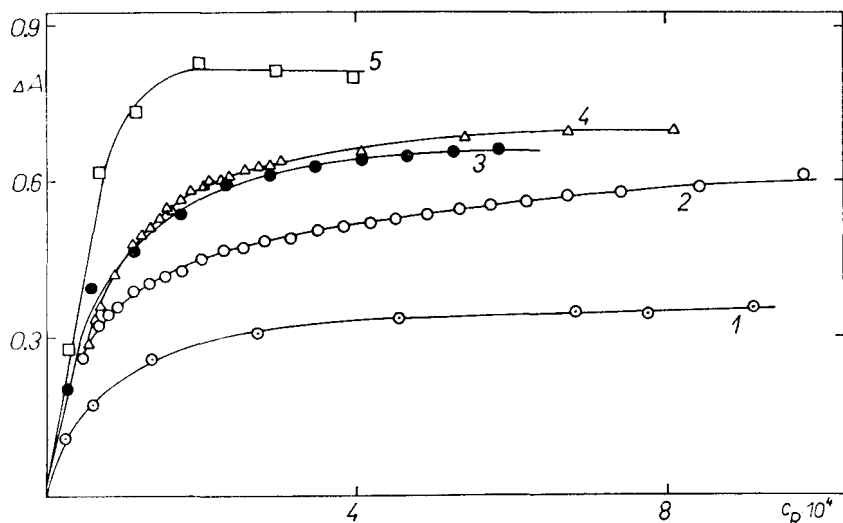


FIG. 8.—Plots of apparent molar absorptivity *vs.* ligand concentration in 30% v/v ethanol at 530 nm, for indium.  
pH: 1—4.130 2—4.60; 3—5.07; 4—5.13; 5—6.07.

accessible pH values and concentrations for the reagent. At  $\lambda_{\max}$  for the complexes the reagent in excess has a relatively high absorbance, so a wavelength of 525–535 nm was selected for measurements. The absorbance of the reagent strongly increases as the pH rises above 5.0, a further reason for choosing pH 5.0–5.2 for the method. Acetate and some other buffers (0.1M) do not influence the absorbance at pH 5.05 but considerably decrease it at lower pH values. Some buffers that do not affect the absorbance do not have adequate buffer capacity at pH 5. A pyridinium perchlorate buffer (0.05–0.1M) does not affect the absorbance at pH 4.15–5.60 and is therefore preferred. The selectivity can be increased by working at lower pH but the concentration of reagent must then be increased. Decreasing the pH below 4.6 is not recommended since the necessary excess of the reagent cannot be added because of the limited solubility of the reagent; the absorbance of the reagent even at 525–530 nm has also to be taken into account. There is some freedom in choice of pH and reagent concentration, but strictly the same conditions must be used for the samples and standards. The Lambert-Beer law is obeyed at 525–530 nm for 0.15–1.6  $\mu\text{g}$  of gallium per ml at pH 4.1–5.6 in solutions containing 30% v/v ethanol and 0.05M pyridine buffer, with constant reagent concentration in the range  $7.24\text{--}3.50 \times 10^{-4}M$ , and up to 2.4  $\mu\text{g}/\text{ml}$  for indium at pH 5.1–6.0 for  $C_R$   $7.24\text{--}4.20 \times 10^{-4}M$ . The apparent molar absorptivities are as follows.

#### Gallium

pH	4.18	4.35	4.60	5.00	5.25	5.55
$C_R, M$	$\leftarrow 7.24 \times 10^{-4}$			$\leftarrow 3.51 \times 10^{-4}$		
$C_R/C_M$	28	32	32	18	18	18
$\epsilon(525 \text{ nm})$	$5.09 \times 10^4$	$5.65 \times 10^4$	$5.72 \times 10^4$	$5.90 \times 10^4$	$5.78 \times 10^4$	$5.68 \times 10^4$
Sensitivity:	0.014–0.012 mg/cm <sup>2</sup> for $A = 0.01$					

#### Indium

pH	4.23	4.60	4.72	4.85	5.06	5.25	5.57	6.04
$C_R, M$	$\leftarrow 7.24 \times 10^{-4}$				$\leftarrow 4.20 \times 10^{-4}$			
$\epsilon(530 \text{ nm})$	$3.08 \times 10^4$	$3.50 \times 10^4$	$3.91 \times 10^4$	$4.40 \times 10^4$	$4.47 \times 10^4$	$5.02 \times 10^4$	$5.25 \times 10^4$	$5.21 \times 10^4$
Sensitivity:	0.037–0.022 mg/cm <sup>2</sup> for $A = 0.01$							

*Procedure*

To 4–10 ml of slightly acid sample ( $\sim 0.1N$  hydrochloric or sulphuric acid) in a 50-ml volumetric flask add 5 ml of 0.003% Pentamethoxyl Red in 96% ethanol and neutralize by dropwise addition of 0.1M ammonia (do not let pH rise above 3.5 or indium will hydrolyse). Add 10 ml of 0.04% (for gallium, 0.047% for indium) w/v solution of TAR in ethanol and 2.5 ml of 1M pyridine buffer (pH 5.0–5.2 for Ga, 5.2–5.3 for In) and dilute to the mark with water. Check that the pH of the solution is the same as that used for the calibration curve. Measure the absorbance after 15 min at 525 or 530 nm against water.

*Precision*

The standard deviation<sup>19</sup> was measured for 10 readings at each of three gallium concentrations and found to be 0.006, 0.005 and 0.007  $\mu\text{g/ml}$  for concentrations of 0.270, 0.674 and 1.078  $\mu\text{g/ml}$  respectively.

*Interferences*

The concentrations of some interfering species causing relative errors of  $\pm 5\%$  in determination of 0.67  $\mu\text{g}$  of gallium ( $C_R = 5.74 \times 10^{-4}M$ ) or 1.53  $\mu\text{g}$  of indium ( $C_R = 6.16 \times 10^{-4}M$ ) per ml at pH 5.0–5.1 and 520 nm are summarized in Table II.

TABLE II.—INTERFERENCE LEVELS

Ion	Tolerance, $\mu\text{g/ml}$		Ion,	Tolerance, $\mu\text{g/ml}$	
	Ga	In		Ga	In
Bi <sup>3+</sup>	0.19	0.20	F <sup>-</sup>	11.8	10.0
Fe <sup>3+</sup>	0.05	0.58	SO <sub>3</sub> <sup>2-</sup>	—	13.6
			PO <sub>4</sub> <sup>3-</sup>	183	4.3
			S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	—	2.5
Zn <sup>2+</sup>	0.36	0.24	MoO <sub>4</sub> <sup>2-</sup>	11.1	15.9
			NO <sub>2</sub> <sup>-</sup>	—	2.9
Cd <sup>2+</sup>	2.51	1.65	WO <sub>4</sub> <sup>2-</sup>	3.5	1.8
			AsO <sub>4</sub> <sup>3-</sup>	—	7.9
Pb <sup>2+</sup>	0.42	0.33	citrate	0.14	0.11
			ascorbinate	*	42.4
Sc <sup>3+</sup>	0.03	0.03	oxalate	0.06	0.09
In <sup>3+</sup>	0.07	—	tartrate	2.4	0.86
Ga <sup>3+</sup>	—	0.03	borate	—	*
UO <sub>2</sub> <sup>2+</sup>	0.24	0.19	sulphosalicylate	85.0	46.9
Zr <sup>4+</sup>	0.04	0.04	phthalate	—	0.57
Th <sup>4+</sup>	0.35	0.47	hypophosphite	*	98.7
			hydrazine	—	124.5
Cu <sup>2+</sup>	0.14	0.12	Y <sup>3+</sup>	0.51	0.23
V <sup>5+</sup>	0.07	0.06	Mn <sup>2+</sup>	48.6	43.5
Er <sup>3+</sup>	0.18	0.12	Be <sup>2+</sup>	8.1	23.4
			Al <sup>3+</sup>	—	56.7

\* No interference by large excess.

The large number of interfering ions severely limits the usefulness of the reagent, but Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, SCN<sup>-</sup>, and hydroxylamine hydrochloride in large excess do not interfere. The interference of Cu<sup>2+</sup> up to 40  $\mu\text{g/ml}$  can be removed by adding 3 ml of 20% w/v sodium thiosulphate solution before the final dilution. Reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup> is without effect since Fe<sup>2+</sup> also interferes strongly.

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**Résumé**—On montre que le gallium réagit avec le TAR pour former les espèces Ga:TAR 1:1 et 1:2, et l'élucidation de leur nature est compliquée par l'hydrolyse. Les espèces  $\text{GaR}^+$  et  $\text{GaHR}(\text{OH})^+$ , où  $\text{H}_2\text{R}$  est le réactif libre, apparaissent à pH 2,7–4,8 pour des solutions qui sont équimolaires ou contiennent un excès d'ion métallique;  $\text{GaHR}^{2+}$  apparaît à pH 2,13–2,86 avec un excès d'ion métallique. Un complexe 1:2, probablement  $\text{GaR}_2^-$ , existe en milieu éthanol aqueux à 30% à pH  $\sim 5$  si un excès de ligand est présent. L'utilité de la réaction pour l'analyse est sévèrement limitée par le grand nombre d'éléments qui interfèrent. L'indium réagit de manière semblable, formant un complexe 1:1 qui est converti dans le complexe 1:2 par un excès de réactif à pH 4,6.

**Zusammenfassung**—Es wird gezeigt, daß Gallium mit TAR zu Spezies mit Ga:TAR = 1:1 und 1:2 reagiert. Ihre Untersuchung wird durch Hydrolyse kompliziert. Die Spezies  $\text{GaR}^+$  und  $\text{GaHR}(\text{OH})^+$ , wo  $\text{H}_2\text{R}$  das freie Reagens bedeutet, kommen bei pH 2,7–4,8 in Lösungen vor, die äquimolare Mengen oder einen Überschuß an Metallionen enthalten; bei pH 2,13–2,86 mit Metallüberschuß findet man  $\text{GaHR}^{2+}$ . Mit Ligandenüberschuß in 30% wäßrigem Äthanol bei pH  $\sim 5$  existiert ein 1:2-Komplex, wahrscheinlich  $\text{GaR}_2^-$ . Der analytische Nutzen der Reaktion ist durch die große Anzahl störender Elemente stark eingeschränkt. Indium reagiert ähnlich und bildet einen 1:1-Komplex, der bei pH 4,6 durch überschüssiges Reagens in den 1:2-Komplex überführt wird.

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## BESTIMMUNG DER FREIEN SÄURE IN PLUTONIUM-, URAN- UND THORIUM- LÖSUNGEN

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**Zusammenfassung**—Es wird ein Verfahren beschrieben zur Bestimmung der freien Säure in Gegenwart von Plutonium, Uran und Thorium. Die Titration erfolgt wegen der leichten Hydrolisierbarkeit der Aktiniden im nichtwäßrigen System (2-Propanol), wobei die Kationen Plutonium, Uran und Thorium durch Zugabe von Cäsiumchlorid als Doppelsalze in 2-Propanol ausgefällt werden. Als Titriermittel wird Natriumäthylat verwendet. Die Äquivalenzpunktsanzeige erfolgt durch Phenolphthalein, wofür neben der visuellen Erkennung auch die Verwendung eines Kolortitrators getestet wurde.

ZUR AUFARBEITUNG und Wiederaufarbeitung der Kernbrennstoffe Plutonium, Uran und Thorium werden meist wäßrige Extraktionsverfahren verwendet. Das Extraktionsverhalten ist stark abhängig von der in den Lösungen vorhandenen freien Säure. Darüber hinaus ist bei höher konzentrierten wäßrigen Plutonium(IV)-Lösungen insofern die genaue Kenntnis der Säurekonzentration von besonderer Wichtigkeit, als in solchen Lösungen bereits im relativ stark sauren Bereich ( $\sim 0.5\text{m HNO}_3$ ) Hydrolyse auftritt, die zur Bildung polymerer Species führt.<sup>1</sup>

Unsere Arbeiten zielten darauf ab, in den bei der Wiederaufarbeitung von Schnell-Brüter-Brennstoffen durch das Purex-Verfahren anfallenden Lösungen die freie Säure genau und auch möglichst schnell, wie es für die Betriebskontrolle notwendig ist, bestimmen zu können. Das bedeutet, daß die freie Säure in Lösungen, die neben Uran(VI), Plutonium(IV) auch Plutonium(III) und Uran(IV) (Uran-Plutonium-Trennkolonne) enthalten, bestimmt werden muß.

Einige Arbeiten beschäftigen sich bereits mit der Bestimmung der freien Säure in wäßrigen Uran(VI)-Lösungen. Bei einem molaren Verhältnis von Säure/Uran  $> 10$  ist die direkte acidimetrische Titration möglich.<sup>2</sup> Ist das Säure/Uran-Verhältnis kleiner, so schlagen verschiedene Autoren die Ausfällung des Urans, z.B. mit Kaliumhexacyanoferrat(III) vor,<sup>3</sup> oder verwenden geeignete Komplexbildner, wie Oxalate,<sup>4-6</sup> Sulfate<sup>7</sup> oder Fluoride.<sup>8,9</sup> Motojima und Izawa<sup>10</sup> u.a. komplexieren das Uran(VI) mit Ammoniumsulfat, titrieren die freie Säure und bestimmen anschließend nach Zugabe von Wasserstoffperoxid das Uran über die freigewordenen  $\text{H}^+$ -Ionen. Eine andere Möglichkeit ergibt sich durch Absorption des Urans an Kationenaustauschern, die mit Wasser bis zur neutralen Reaktion eluiert werden.<sup>13</sup> Für sehr kleine molare Verhältnisse  $\text{H}^+/\text{UO}_2^{2+}$  wird eine Methode beschrieben, bei der in wäßrigen Lösungen von Natriumnitrat oder Natriumchlorid in Anwesenheit von n-Tributylphosphat (Extraktion der Uranyl-nitrate) die freie Säure titriert wird.<sup>14</sup>

Weit weniger Publikationen liegen über die Bestimmung der freien Säure in plutoniumhaltigen Lösungen vor. Einerseits ist dies auf die starke Hydrolyseneigung des Plutonium(IV) im Vergleich zu anderen Aktiniden der Oxidationsstufe IV und VI zurückzuführen, wie es durch die folgenden Hydrolysegleichungen und  $pK_h$ -Werte grob veranschaulicht wird:

		Ref.
$pK_h \sim 3,4;$	$\text{Th}^{4+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Th}(\text{OH})^{3+} + \text{H}_3\text{O}^+$	32
$pK_h \sim 0,7;$	$\text{U}^{4+} + \text{H}_2\text{O} \rightleftharpoons \text{U}(\text{OH})^{3+} + \text{H}^+$	33
$pK_h \sim 6;$	$2\text{UO}_2^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{U}_2\text{O}_5^{2+} + 2\text{H}^+$	34
$pK_h \sim 7,3;$	$\text{Pu}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{Pu}(\text{OH})^{2+} + \text{H}^+$	35
$pK_h \sim 5,7;$	$\text{PuO}_2^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{PuO}_2(\text{OH})^+ + \text{H}^+$	15
$pK_h \sim 0,7^*;$	$\text{Pu}^{4+} + \text{H}_2\text{O} \rightleftharpoons \text{Pu}(\text{OH})^{3+} + \text{H}^+$	33

\* extrapoliert auf Ionenstärke 0.

Andererseits treten in wäßrigen Lösungen infolge der geringen Unterschiede in den Redoxpotentialen, besonders bei niedrigen Säurekonzentrationen, die Oxidationsstufen III, IV und VI des Plutoniums nebeneinander auf. Diese Tatsachen komplizieren die Maskierung des Hydrolyseeinflusses vom Plutonium während der acidimetrischen Titration.

Von Pflug und Miner<sup>11</sup> wurde eine Methode beschrieben, die für geringe Plutoniumkonzentrationen den Hydrolyseeinfluß durch Komplexierung mit Citrat oder Oxalat verhindert. In den Wiederaufarbeitungs-Anlagen von Windscale und Eurochemic-Mol<sup>12</sup> wird Plutonium(IV) mit Natriumfluorid ausgefällt und so maskiert. Für die Bestimmung der freien Säure neben hohen Plutoniumkonzentrationen wurden Methoden beschrieben, die das Plutonium durch Ausfällen als Plutoniumjodat maskieren. Smith<sup>16</sup> schlägt Kaliumjodat als Fällungsreagenz vor. Thiele und Bähr<sup>17</sup> modifizierten dieses Verfahren, da sie schon bei Plutoniumkonzentrationen von <30 mg/ml erhebliche positive Fehler erhielten, in der Art, daß sie statt Kaliumjodat zur Ausfällung des Plutoniums Jodsäure verwendeten. Für 0,9m Plutoniumlösungen ( $\text{H}^+/\text{Pu} = 2,5$ ) erhielten sie dabei Fehler von rund 4%. Für kleine Plutoniumkonzentrationen (bis zu 0,3m), jedoch in Anwesenheit von Uran (bis zu 0,8m), welches durch Ammoniumsulfat komplexiert wurde, verringerte sich der Fehler auf 1-2%.<sup>18</sup>

Damien und Cauchetier<sup>19</sup> maskieren das Plutonium durch Komplexierung mit EDTA. Das Verfahren ist nur für einen engen Säurebereich geeignet und wird schon durch 10 mg Uran in der Probe gestört. Vogg<sup>20</sup> diskutiert eine Möglichkeit zur Bestimmung der freien Säure in Plutonium(IV)-Lösungen durch Oxidation des  $\text{Pu}^{4+}$  zu  $\text{PuO}_2^{2+}$ . Die freie Säure kann dann direkt oder bei höheren  $\text{PuO}_2^{2+}$ -Konzentrationen nach Komplexierung mit Ammoniumsulfat neben  $\text{PuO}_2^{2+}$  titriert werden.<sup>21</sup>

Nach Kraus und Dam<sup>22</sup> kann auch in Lösungen, die  $\text{Pu}^{3+}$  enthalten, die freie Säure, zumindest bei kleinen  $\text{Pu}(\text{III})$ -Konzentrationen, direkt (ohne Maskierung) titriert werden. Bähr und Thiele<sup>23</sup> erhielten auch für höhere  $\text{Pu}(\text{III})$ -Konzentrationen (bis zu 15 mg  $\text{Pu}/\text{Probe}$ ) ohne Zusatz von Komplexbildnern von der Hydrolyse unbeeinflusste Ergebnisse.

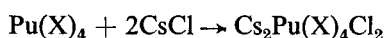
Für die Bestimmung der freien Säure in Lösungen, die Thorium(IV) enthalten, wird die Verwendung von Kaliumoxalat als Komplexbildner vorgeschlagen.<sup>24,25</sup> Außerdem ergibt sich die Möglichkeit nach Verdünnung bzw. Neutralisation der Lösung über pH-Messung im Vergleich mit Standardlösungen quantitative Aussagen über den Gehalt an freier Säure zu machen.<sup>24</sup>

Für die Säurebestimmung in Uran(IV)-Lösungen fanden wir keine Hinweise in der Literatur.

Eine Versuchsreihe, in verschiedenen hochkonzentrierten Salzlösungen  $[(\text{NH}_4)_2\text{SO}_4, \text{NH}_4\text{NO}_3, \text{KNO}_3, \text{LiCl}$  usw.], die freie Säure in Gegenwart von Thorium(IV) und Plutonium(IV) zu bestimmen, verlief unbefriedigend. Erst nach Verwendung von Alkohol als Lösungsmittel verbesserten sich die Ergebnisse, insbesondere im Hinblick auf die Erkennung des Äquivalenzpunktes. Außerdem setzten wir einer gesättigten Ammoniumsulfatlösung Cäsiumchlorid zu und fällten durch Zugabe von Methanol die Salze aus. Dadurch konnte anschließend die freie Säure neben Plutonium(IV) mit einer alkoholischen Natronlauge titriert werden. Bei dieser Verfahrensweise zeigten sich jedoch durch das alkoholische Medium erhebliche Schwierigkeiten, hervorgerufen von den großen Mengen an Salzniederschlag und durch Funktionsstörungen der verwendeten Glas-Kalomel Elektrodenmeßkette.

Nach einer großen Zahl von Variationen erwies sich für die Bestimmung der freien Säure neben  $\text{UO}_2^{2+}$ ,  $\text{U}^{4+}$ ,  $\text{Pu}^{3+}$ ,  $\text{Pu}^{4+}$  und  $\text{Th}^{4+}$  (Metallkonzentrationen bis zu 1m) folgendes Verfahren am geeignetsten.

Die in 2-Propanol gering löslichen Doppelsalze der hydrolysierbaren Kationen werden durch Zugabe eines Überschusses von Cäsiumchlorid ausgefällt.<sup>26,27</sup>



In einem Volumen von 30 ml 2-Propanol, worin 50 mg Plutonium mit 1,5 g CsCl ausgefällt worden waren, lösten sich nur 6  $\mu\text{g}$  Plutonium. Nach der Titration mit  $\text{NaOC}_2\text{H}_5$  erhöht sich die Löslichkeit nur unwesentlich (Pu 9  $\mu\text{g}/30$  ml).

Als Titrationsmittel verwenden wir, um keine zusätzlichen  $\text{OH}^-$ -Ionen einzubringen, in 2-Propanol gelöstes Natriumäthylat. Zur Endpunktsanzeige erwies sich bei unseren Versuchen und insbesondere für Serienanalysen die Verwendung von Phenolphthalein als Indikator am geeignetsten.

## EXPERIMENTELLER TEIL

### Geräte

Metrohm-Potentiograph E 336 mit Kolortitratator E 1018; Kolbenbürette 5 oder 10 ml.

Radiometer-Titrierapparatur bestehend aus: Auto-Bürette ABU 1b, mit 2,5 ml Bürette, Titriograph SBR 2c, Titrator 11, pH-Meter 28 und photometrische Titriereinrichtung TTA4.

Alle titriermittelführenden Leitungen sollten aus Teflon oder Polyäthylen (nicht aus Polyvinylchlorid) sein.

### Chemikalien

2-Propanol, p.a.

Cäsiumchlorid, p.a.

Natriumäthylat, pract.

1%ige Phenolphthalein-Lösung in Alkohol

*Herstellung der Natriumäthylat-Lösung.* Natriumäthylat-Pulver wird in siedendem 2-Propanol gelöst. Ungelöste Anteile werden, nachdem die Lösung im Kühlschrank abgekühlt wurde, abfiltriert. Erfahrungsgemäß zeigen diese Lösungen nach einigen Tagen eine Trübung, weshalb täglich Kontrolltitrationen durchgeführt werden sollten. Bei starker Trübung oder gar Ausfällung muß filtriert werden. Die Lösung sollte nicht stärker als 0,2m angesetzt werden, da bei größeren Konzentrationen die Stabilität der Lösungen schlechter wird.

### Säurestandard-Lösungen

*Plutonium(IV)-sulfat-Lösungen.* Das Plutonium(IV)-sulfat wurde nach einem von Pietri beschriebenen Verfahren hergestellt.<sup>28,29</sup> Die coulometrische Bestimmung des Plutoniumgehaltes der Substanz

ergab eine Abweichung von <0,5% vom theoretischen Wert. Die Standardlösungen wurden durch Zugabe einer genau definierten Menge Schwefelsäure hergestellt.

**Plutonium(IV)-nitrat-Lösungen.** Erfahrungsgemäß ist die Herstellung konzentrierter Plutonium(IV)-nitratlösungen sehr schwierig, da es z.B. unsicher ist, durch Ausfällung exakt stöchiometrisches Plutonium(IV)-hydroxid zu erhalten, welches nach Auflösung in einer definierten Menge Salpetersäure die genaue Berechnung der freien Säure zuläßt. Für die Herstellung unserer Plutonium(IV)-nitratlösungen wurde Plutoniummetall in Salzsäure gelöst und das entstandene Plutoniumchlorid als Peroxid ausgefällt. Nach mehrmaligem Waschen wurde der Niederschlag in 10m Salpetersäure aufgelöst. Durch dieses Verfahren ist die Säurekonzentration der Lösung jedoch nicht genau bestimmt.

**Plutonium(III)-chlorid-Lösungen.** Nachdem Plutoniumchlorid durch Chlorierung von  $\text{PuO}_2$  im  $\text{CCl}_4\text{-Cl}_2$ -Argon-Strom hergestellt und anschließend sublimiert worden war,<sup>30</sup> wurden von dieser Substanz Lösungen mit genau definierter Menge Salzsäure hergestellt.

**Uranylнитrat-Lösungen.** Die Uranylнитratlösungen wurden entweder direkt durch Auflösung von  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , *p.a.*, in einer definierten Salpetersäuremenge hergestellt oder das Uranylнитrat wurde mit einer Chloroform-Wäsche und anschließender Trocknung im Vakuum über NaOH vorbehandelt.

**Uran-IV-nitrat-Lösungen.** Die salpetersauren Uran(IV)-nitrat-Lösungen wurden durch elektrolytische Reduktion hergestellt.<sup>31</sup> Der Gehalt an freier Säure in diesen Lösungen ist nicht bekannt.

**Thoriumnitrat-Lösungen.**  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$  *p.a.* wurde entweder direkt, oder nach ähnlicher Vorbehandlung wie bei den Uranylнитrat-Lösungen beschrieben, in genau definierten Mengen Salpetersäure gelöst.

### Titration

Ein aliquoter Teil der Probe (Metallmenge  $\leq 60$  mg, Volumen  $\leq 1$  ml) wird abgenommen und in den Titrierbecher gegeben. Danach wird mit  $\sim 1,5$  g gemörsertem Cäsiumchlorid überschichtet. Anschließend werden 30 ml 2-Propanol sowie 2–3 Tropfen Phenolphthalein-Lösung zugegeben. Es wird sowohl bei der visuellen Erkennung des Phenolphthalein-Umschlages, wie auch bei der Verwendung von Glas-Kalomel Elektroden-Meßketten in einem 50-ml Becherglas mit einem kräftigen Magnetrührer gearbeitet. In jedem Fall muß darauf geachtet werden, daß eine möglichst homogene Suspension entsteht und keine Salzkrusten an der Wandung des Titrierbeckers haften bleiben. Die Titrierspitze wird in die Lösung eingetaucht und es wird bis zum deutlichen Umschlag von farblos nach rot titriert. Die Umschlagsnähe kündigt sich durch die Bildung von rosa Schlieren an. Erfahrungsgemäß muß ein Blindwert berücksichtigt werden, der für die angegebenen Bedingungen *ca.* 0,03 ml Titriermittel beträgt.

## ERGEBNISSE

Für 25 Titrationsen einer 0,974m Salpetersäure im beschriebenen System ergab sich bei Anwendung des Kolortitrators zur Endpunktanzeige und 0,500 bzw. 0,100 ml Probenvolumen eine relative Standardabweichung von 0,9%.

Tabelle I zeigt die Titrationsergebnisse der Säurestandardlösungen in Anwesenheit von Plutonium(IV)-sulfat. Die relativen Standardabweichungen sind aus mindestens

TABELLE I.—TITRATIONEN DER SÄURESTANDARDLÖSUNGEN IN ANWESENHEIT VON PLUTONIUM(IV)-SULFAT

Lösung	Pu eingesetzt, <i>mÄq</i>	H <sup>+</sup> , <i>mÄq</i>	
		eingesetzt	gefunden*
0,959n H <sub>2</sub> SO <sub>4</sub> –0,26m Pu(SO <sub>4</sub> ) <sub>2</sub>	0,21	0,192	0,194†
0,959n H <sub>2</sub> SO <sub>4</sub> –0,26m Pu(SO <sub>4</sub> ) <sub>2</sub>	0,11	0,096	0,098†
0,960n H <sub>2</sub> SO <sub>4</sub> –0,22m Pu(SO <sub>4</sub> ) <sub>2</sub>	0,22	0,240	0,237‡
0,480n H <sub>2</sub> SO <sub>4</sub> –0,487m HNO <sub>3</sub> –0,11m Pu(SO <sub>4</sub> ) <sub>2</sub>	0,09	0,193	0,196‡
0,480n H <sub>2</sub> SO <sub>4</sub> –1,54m HNO <sub>3</sub> –0,11m Pu(SO <sub>4</sub> ) <sub>2</sub>	0,09	0,404	0,405‡
0,480n H <sub>2</sub> SO <sub>4</sub> –2,57m HNO <sub>3</sub> –0,11m Pu(SO <sub>4</sub> ) <sub>2</sub>	0,09	0,610	0,605‡

\* Standardabweichung wurde zu 1,2% ermittelt.

† Endpunktsanzeige mit Glas-Kalomel-Meßkette.

‡ Endpunktsanzeige mit Phenolphthalein (visuell).

10 Titrationen ermittelt, wobei auch über Ergebnisse mit unterschiedlichen Proben-  
volumina gemittelt wurde.

In Tabelle II sind die Titrationsergebnisse der Plutoniumnitratlösungen zusam-  
mengefaßt. Die Lösungen wurden parallel auch nach der Methode von Thiele und  
Bähr<sup>17</sup> bestimmt. Die Titrationen in den letzten beiden Reihen der Tabelle wurden  
mit dem Kolortitrator von Radiometer ausgeführt.

TABELLE II.—TITRATIONEN VON SALPETERSÄURESTANDARDLÖSUNGEN IN  
ANWESENHEIT VON PLUTONIUM(IV)-NITRAT

Lösung	Pu eingesetzt, <i>mÄq</i>	H <sup>+</sup> , <i>mÄq</i>	
		eingesetzt	gefunden*
3,33m HNO <sub>3</sub> -0,97m Pu(NO <sub>3</sub> ) <sub>4</sub>	0,19	0,166†	0,162‡
3,33m HNO <sub>3</sub> -0,97m Pu(NO <sub>3</sub> ) <sub>4</sub>	0,39	0,333†	0,331‡
3,33m HNO <sub>3</sub> -0,97m Pu(NO <sub>3</sub> ) <sub>4</sub>	0,97	0,833†	0,820‡
3,56m HNO <sub>3</sub> -1,12m Pu(NO <sub>3</sub> ) <sub>4</sub>	0,45	0,356†	0,348‡
3,56m HNO <sub>3</sub> -1,12m Pu(NO <sub>3</sub> ) <sub>4</sub> 1:1 verdünnt mit 0,974m HNO <sub>3</sub>	0,45	0,445	0,450‡
3,56m HNO <sub>3</sub> -1,12m Pu(NO <sub>3</sub> ) <sub>4</sub> 1:1 verdünnt mit 3,08m HNO <sub>3</sub>	0,45	0,656	0,647‡
3,56m HNO <sub>3</sub> -1,12m Pu(NO <sub>3</sub> ) <sub>4</sub>	0,45	0,356†	0,349§
3,56m HNO <sub>3</sub> -1,12m Pu(NO <sub>3</sub> ) <sub>4</sub>	0,90	0,712†	0,697§

\* Die Standardabweichung wurde zu 1,1 % ermittelt.

† durch HJO<sub>3</sub>-Methode<sup>17</sup> bestimmt.

‡ Endpunktsanzeige mit Phenolphthalein (visuell).

§ Endpunktsanzeige mit Phenolphthalein (Kolortitrator Radiometer).

Tabelle III zeigt die Ergebnisse der Titrationen neben Uranylнитrat, und in der  
letzten Spalte neben Uranylнитrat und Plutonium(IV)-nitrat. Das Uranylнитrat wurde,  
wie vorher beschrieben, vorbehandelt. Lösungen die aus nicht vorbehandeltem  
Uranylнитrat hergestellt wurden, ergaben einen einheitlich höheren Säuregehalt von  
~2,8 mÄq Säure pro 100 mÄq Uran.

TABELLE III.—TITRATIONEN VON SALPETERSÄURELÖSUNGEN IN  
ANWESENHEIT VON URANYLNITRAT

Lösung	UO <sub>2</sub> <sup>2+</sup> eingesetzt, <i>mÄq</i>	H <sup>+</sup> , <i>mÄq</i>	
		eingesetzt	gefunden*
0,513m HNO <sub>3</sub> -0,4m UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	0,40	0,256	0,254†
0,881m HNO <sub>3</sub> -0,8m UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	0,40	0,220	0,218†
4,58m HNO <sub>3</sub> -0,8m UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	0,40	1,14	1,14†
4,58m HNO <sub>3</sub> -0,8m UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	0,40	1,144	1,150‡
2,47m HNO <sub>3</sub> -0,8m UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	0,16	0,246	0,245‡
2,88m HNO <sub>3</sub> -0,49m Pu(NO <sub>3</sub> ) <sub>4</sub> -0,40m UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	0,20 Pu <sup>4+</sup> 0,08 UO <sub>2</sub> <sup>2+</sup>	0,287	0,290†

\* Die Standardabweichung wurde zu 1 % ermittelt.

† Endpunktsanzeige mit Phenolphthalein (visuell).

‡ Endpunktsanzeige mit Phenolphthalein (Kolortitrator, Metrohm).

Zur Überprüfung der Säurebestimmung neben Plutonium(III)-chlorid wurden  
salzsaure Lösungen hergestellt und titriert. Tabelle IV zeigt die Ergebnisse.

TABELLE IV.—TITRATIONEN VON SALZSÄURESTANDARDLÖSUNGEN IN ANWESENHEIT VON PLUTONIUM(III)-CHLORID

Lösung	Pu eingesetzt, <i>mÄq</i>	H <sup>+</sup> , <i>mÄq</i>	
		eingesetzt	gefunden*
0,807m HCl-0,80m PuCl <sub>3</sub>	0,60	0,202	0,205†
4,00m HCl-0,80m PuCl <sub>3</sub>	0,60	1,00	1,00†

\* Die Standardabweichung wurde zu 1% ermittelt.

† Endpunktsanzeige mit Phenolphthalein (visuell).

Tabelle V und VI zeigen die Titrationsergebnisse der Thoriumnitrat-bzw. der Uran(IV)-nitrat-Lösungen. Zur Endpunktbestimmung wurde bei diesen Titrationen neben der visuellen Erkennung auch der Kolortitratator von Metrohm verwendet.

TABELLE V.—TITRATIONEN VON SALPETERSÄURESTANDARDLÖSUNGEN IN ANWESENHEIT VON THORIUM

Lösung	Th <sup>4+</sup> eingesetzt, <i>mÄq</i>	H <sup>+</sup> , <i>mÄq</i>	
		eingesetzt	gefunden*
4,38m HNO <sub>3</sub> -0,8m Th(NO <sub>3</sub> ) <sub>4</sub>	0,80	1,09	1,11†
4,38m HNO <sub>3</sub> -0,8m Th(NO <sub>3</sub> ) <sub>4</sub>	0,80	1,09	1,08§
HNO <sub>3</sub> unbestimmt-0,8m Th(NO <sub>3</sub> ) <sub>4</sub>	0,80		0,277†
0,609m HNO <sub>3</sub> -0,4m Th(NO <sub>3</sub> ) <sub>4</sub> ‡	0,80	0,305	0,309†
1,040m HNO <sub>3</sub> -0,4m Th(NO <sub>3</sub> ) <sub>4</sub> ‡	0,80	0,520	0,530†

\* Die Standardabweichung wurde zu 1,3% ermittelt.

† Endpunktsanzeige mit Phenolphthalein (visuell).

‡ Die Lösungen wurden durch Verdünnung der unbestimmten Th(NO<sub>3</sub>)<sub>4</sub>-Lösung mit bekannter Säure hergestellt.

§ Endpunktsanzeige mit Phenolphthalein (Kolortitratator, Metrohm).

TABELLE VI.—TITRATIONEN VON SALPETERSÄURE IN ANWESENHEIT VON URAN(IV)-NITRAT

Lösung	U <sup>4+</sup> eingesetzt, <i>mÄq</i>	H <sup>+</sup> , <i>mÄq</i>	
		eingesetzt	gefunden*
HNO <sub>3</sub> unbestimmt-0,89m U(NO <sub>3</sub> ) <sub>4</sub>	0,89		0,511†
HNO <sub>3</sub> unbestimmt-0,89m U(NO <sub>3</sub> ) <sub>4</sub>	1,78		1,02†
1,51m HNO <sub>3</sub> -0,45m U(NO <sub>3</sub> ) <sub>4</sub> ‡	0,36	0,301	0,305†
3,59m HNO <sub>3</sub> -0,45m U(NO <sub>3</sub> ) <sub>4</sub> ‡	0,36	0,719	0,721†

\* Die Standardabweichung wurde zu 1,3% ermittelt.

† Endpunktsanzeige mit Phenolphthalein (visuell).

‡ Die Lösungen wurden durch Verdünnung der unbestimmten U(NO<sub>3</sub>)<sub>4</sub>-Lösung mit bekannter Säure hergestellt.

Die direkte Bestimmung der freien Säure im Purex-Extraktionsmittel n-Tributylphosphat, verdünnt mit Dodecan, ist nach diesem Verfahren nicht möglich. Die Endpunktsanzeige durch Phenolphthalein ist in Anwesenheit von n-TBP gestört. Die Ergebnisse liegen zu hoch. In Tabelle VII sind die Versuche zusammengestellt, bei denen mit gesättigter wäßriger Cäsiumchlorid-Lösung mehrmals gestript wurde.

Der Gehalt an freier Säure in den organischen Proben wurde aus dem Gehalt in den Ansatzlösungen und dem Gehalt in den anorganischen Phasen nach der Extraktion mit 20 V% n-TBP-Dodecan berechnet.

TABELLE VII

Probe		Analyse	
$\text{UO}_2^{3+}$ <i>mÄq</i>	$\text{H}^+$ errechnet, <i>mÄq</i>	$\text{H}^+$ gefunden,* <i>mÄq</i>	relative Standardabweichung
—	0,070	0,069	~2%
—	0,374	0,369	~1%
0,30	0,059	0,058	~5%
0,15	0,340	0,341	~2%

\* Endpunktsanzeige mit Phenolphthalein (visuell).

Zur Überprüfung des Einflusses von Eisen(III) auf die Bestimmung wurden zwei 0,05m Eisen(III)-Ammoniumsulfat-Lösungen hergestellt, die 0,49m bzw. 2,58m an freier Salpetersäure waren. Die Titrationsergebnisse zeigten, daß die Methode durch Eisen(III) in diesen Konzentrationen nicht gestört wird.

## DISKUSSION

Auf Grund der genannten Schwierigkeit bei der Herstellung von Plutonium(IV)-nitrat-Lösungen mit genau bekanntem Säuregehalt beschränken wir uns für die Beurteilung der Genauigkeit auf folgende Schlüsse: (a) Analogie mit den Titrationen der genau bestimmten Plutoniumsulfat-Lösungen; (b) wenn die Hydrolyse die Bestimmung beeinflussen würde, müßte bei Anwendung von unterschiedlichen Probevolumina und variierten  $\text{H}^+/\text{Pu}$ -Verhältnissen der Hydrolyseeinfluß in den Ergebnissen sichtbar werden; das ist nicht der Fall, wie aus Tabelle II zu ersehen ist; (c) das Verfahren wurde mit der Jodsäure-Methode<sup>17</sup> verglichen und zeigt gute Übereinstimmung, wie die Werte der Tabelle II zeigen.

Ganz ähnlich liegt die Situation bei der Bestimmung der freien Säure in Uran(IV)-nitrat-Lösungen. Darüberhinaus besteht beim Uran(IV) die Möglichkeit, daß während der Titration eine teilweise Oxidation zum Uran(VI) eintritt, wodurch die Säurebestimmung verfälscht würde. Versuche mit 2-Propanol, welches über Natronlauge und Eisen(II) destilliert wurde, und Einleiten von Stickstoff während der Titration bestätigen jedoch diesen Verdacht nicht. Wurden die Titrationen unter Kühlung durchgeführt (5°), so zeigte sich im Gegenteil eine kleine Erhöhung des Natriumäthylatverbrauches.

Zur Erkennung des Äquivalenzpunktes fanden wir Phenolphthalein-Indikator am geeignetsten, obwohl der Farbumschlag nur kurze Zeit (20 sec) anhält und dadurch die Gefahr des Übertitrierens gegeben ist. Die gute Übereinstimmung der visuell bestimmten Ergebnisse mit denen, die mit dem Kolortitrator von Metrohm und der photometrischen Titriereinrichtung von Radiometer ausgeführt wurden, sowie die Reproduzierbarkeit von ca. 1%, erweisen die gewählte Methode jedoch als hinreichend genau.

Versuche mit einer Leitfähigkeits-Meßzelle von Radiometer erwiesen sich als wenig geeignet, da eine sichere Endpunktserkennung stark vom Wassergehalt im System, d.h. vom Probenvolumen abhängig ist.



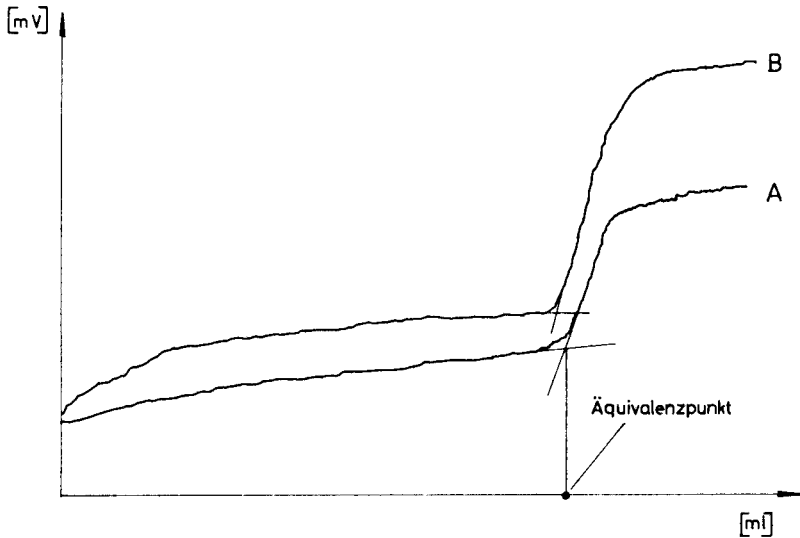


ABB. 1.—(A) Titrationskurve eines Metrohm-Kolortitrators, 1 mV/mm.  
(B) Titrationskurve eines Radiometer-Kolortitrators, 1 mV/mm.

Abbildung 1 zeigt typische Titrationskurven, wie sie bei Verwendung des Radiometer- und Metrohm-Kolortitrators erhalten werden. Die relativ kleinen Sprünge am Äquivalenzpunkt sind auf die starken Trübungen der Lösungen zurückzuführen.

In der Abb. 2 ist der Titrationsverlauf, wie er bei Verwendung einer Glaselektrode S-30050/17 und einer Kalomelelektrode S-30080/17 der Fa. Schott erhalten wird, dargestellt. Die zweite Kurve der Abb. 2 zeigt den Verlauf mit einer Einstabmeßkette

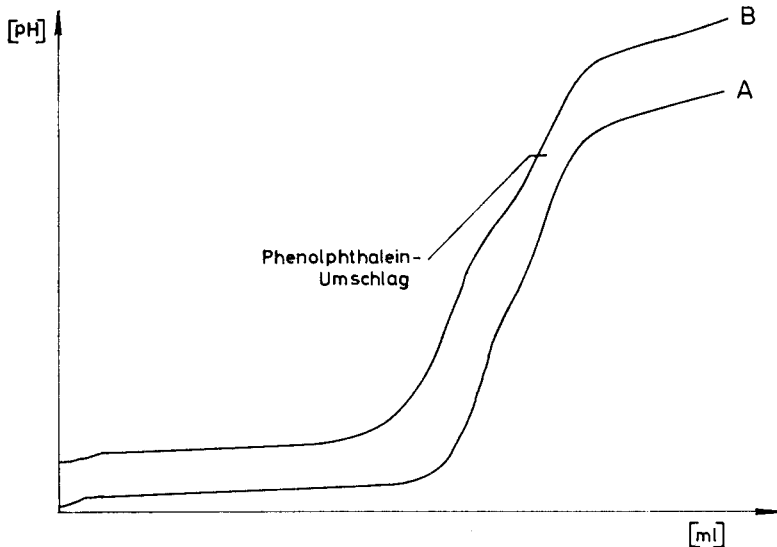


ABB. 2.—(A) Titrationskurve mit Glas- und Kalomel-Elektroden; [Elektrolytschlüssel  $(\text{NH}_4)_2\text{SO}_4$  in  $\text{CH}_3\text{OH}$ ; Fa. Schott].  
(B) Titrationskurve mit Einstabmeßkette UX (Fa. Metrohm).

UX von Metrohm. Die verwendeten Elektroden zeigten schon nach kurzem Gebrauch in 2-Propanol Funktionsstörungen, die sich durch unscharfen Umschlag und erhöhten Titrationsmittelverbrauch bemerkbar machten. Wahrscheinlich ist es jedoch möglich durch geeignete Auswahl und spezielle Behandlung Elektroden zu finden, die für die Methode geeignet sind.

Wir danken Herrn Prof. Dr. F. Baumgärtner für die Anregung zu dieser Arbeit. Herrn U. Lamek danken wir für seine wertvolle Mitarbeit bei den Experimenten. Herrn Dr. B. Kanellakopoulos und Herrn Dr. E. Schwind haben wir für die Herstellung des Plutonium(III)-chlorid, bzw. der Uran(IV)-nitrat-Lösungen zu danken.

**Summary**—A method for the determination of free acid in the presence of plutonium, uranium and thorium is described. Since the actinides easily undergo hydrolysis, the titration is performed in a non-aqueous system (2-propanol). Plutonium, uranium and thorium are precipitated as double salts by the addition of caesium chloride. Sodium ethoxide is used as titrant, with phenolphthalein serving as a visual indicator. A photometric titrator has also been tested.

**Résumé**—On décrit une méthode pour le dosage d'acide libre en présence de plutonium, uranium et thorium. Etant donné que les actinides sont aisément hydrolysables, le titrage est effectué dans un système non aqueux (2-propanol). Le plutonium, l'uranium et le thorium sont précipités à l'état de sels doubles par l'addition de chlorure de caesium. On utilise l'éthoxyde de sodium comme agent de titrage, la phénolphthaléine servant d'indicateur visuel. On a aussi essayé un appareil de titrage photométrique.

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## CONTRIBUTION AU DOSAGE DU GLYCEROL DANS LES GLYCERINES TECHNIQUES—II\*

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**Résumé**—Les auteurs apportent la confirmation expérimentale de l'hypothèse de la volatilisation d'acide formique au cours du dosage volumétrique du glycérol au periodate. Ils proposent d'améliorer la reproductibilité des titres en effectuant ceux-ci en présence de formiate de sodium.

RAPPELONS que l'oxydation du glycérol, à froid, par le periodate de sodium en milieu acide fort, aboutit à la formation d'acide formique en quantité équivalente. Le titrage de ce dernier par l'hydroxyde de sodium, en utilisant un pH-mètre pour déterminer le point final, permet de déduire la teneur en glycérol de l'échantillon analysé en tenant compte du résultat d'un essai à blanc effectué parallèlement.

Dans une précédente communication,<sup>1</sup> Mormont et Gillet ont montré que la méthode officielle de dosage, basée sur ce principe et publiée par l'U.I.C.P.A.,<sup>2</sup> est entachée d'une erreur systématique explicable par l'hypothèse d'une perte d'acide formique, celui-ci étant volatilisé en cours d'opération. La mise en évidence de cette perte justifiait, *a posteriori*, la correction empirique actuellement appliquée au résultat en arrêtant le titrage de l'essai à blanc au pH 6,5 alors que celui du dosage est poursuivi jusqu'au pH 8,1.

L'hypothèse émise, difficilement vérifiable par les techniques simples de laboratoire, a rencontré entretemps un certain scepticisme, ce qui a amené les auteurs à poursuivre l'étude avec la collaboration des experts† chargés, dans le cadre de l'ISO (TC 47/GT 2), de l'élaboration d'une norme internationale applicable aux produits techniques.

Ces travaux non seulement apportent la confirmation expérimentale de l'hypothèse émise, mais encore permettent de définir dans le détail les différents paramètres de la méthode et de proposer ici une version de cette dernière, améliorée par l'introduction de formiate de sodium dans les préparations en vue d'uniformiser le point final des titrages et de le stabiliser.

### *La perte d'acide formique*

Rappelons tout d'abord que l'hypothèse de la perte d'acide formique par volatilisation repose sur une observation simple: Du fait de la nature exothermique des

\* Communication I—voir référence 1.

† Certains essais ont notamment été effectués dans les laboratoires de la firme Procter and Gamble Ltd à Newcastle et à Londres, à l'intervention de R. F. Barbour. Nous tenons à lui en exprimer ici notre gratitude.

réactions d'oxydation en jeu, un peu d'eau s'évapore des préparations et se condense partiellement sous forme de buée, sous les verres de montre couvrant les bechers, pendant les repos qui sont relativement longs. Mises au contact d'un papier indicateur de pH, ces buées se révèlent acides dans le cas de l'échantillon (pH env. 3) et neutres dans le cas de l'essai à blanc (pH env. 6,5). Nous avons déjà montré en outre<sup>1</sup> que le titre alcalimétrique de la préparation elle-même diminue au fil du temps dans des proportions mesurables. Restait à prouver qu'il s'agissait bien d'une volatilisation d'acide formique. Nous y sommes parvenus de la façon suivante.

Les quantités fixées dans la buée, sous les verres de montre, ne pouvaient représenter qu'une fraction de la perte, elle-même peu importante: 0,1 à 0,3% du titre net, en valeur absolue, si on l'apprecie par la valeur de la correction appliquée. Il

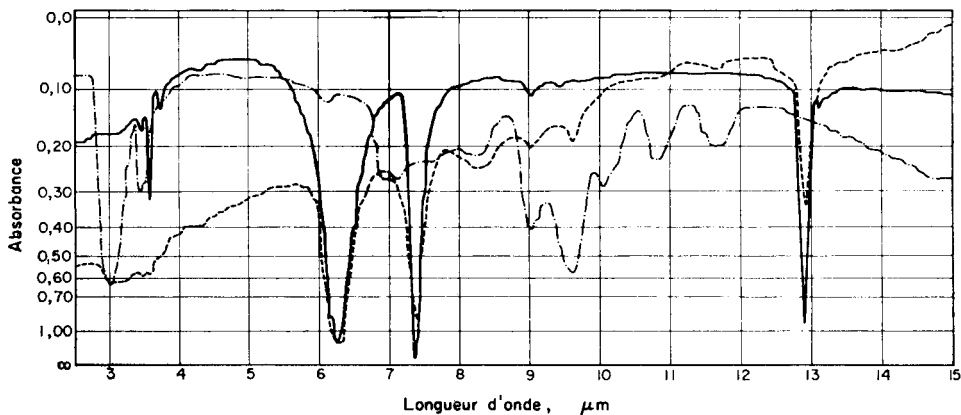


FIG. 1.—Spectres d'absorption I.R.  
 ———: formiate de Na — . . . : glycérol — — — —: condensat recueilli sous le verre de  
 montre couvrant la préparation pendant le dosage

était illusoire dans ces conditions de chercher un moyen de caractérisation chimique des traces d'acide formique éventuellement présentes. Par contre, le spectre d'absorption I.R. du formiate de sodium est bien connu. Nous avons donc tenté de le comparer à celui du condensat en recueillant par rinçage les buées de plusieurs préparations afin de disposer d'un échantillon suffisamment important. Celui-ci, neutralisé par l'hydroxyde de sodium, a fourni le spectre d'absorption I.R. représenté au diagramme de la figure 1.

La présence d'un pic caractéristique, à la longueur d'onde de 12,9  $\mu\text{m}$  ne laisse aucun doute sur la présence d'acide formique dans les condensats examinés. On note, en outre, que des traces de glycérol interviennent dans l'absorption I.R., probablement entraînées par la vapeur d'eau au cours des premiers instants de la réaction.

La quantité d'acide formique récupérable sur le verre de montre a été déterminée par combinaison et titration des buées de 38 dosages simultanés; titre net 2,236 ml de NaOH 0,01N; titre par préparation 0,059 ml, équivalent à 0,01% en glycérol. Naturellement c'est impossible de récupérer tout l'acide formique perdu; on récupère  $\sim 10\%$  de la perte totale.

#### *Le phénomène compensatoire des erreurs systématiques*

Ainsi qu'il a été signalé précédemment,<sup>1</sup> le fait d'arrêter le titre de l'essai à blanc au pH 6,5 équivalait à faire abstraction de l'acide carbonique dissous et des acides

faibles éventuellement apportés par les réactifs, titrés par ailleurs lors du dosage et comptés par conséquent comme glycérol dans le calcul du titre net. La correction systématique ainsi effectuée compense, semble-t-il, la perte d'acide formique établie plus haut. Nous avons, à l'époque, suggéré une modification mineure du mode opératoire permettant pratiquement d'éviter cette perte. Elle consiste à diluer les préparations au début des opérations et non plus avant le titre final.

Son application a montré, entretemps, que la dilution préalable a un effet secondaire, non négligeable, qui n'avait pas été senti à l'époque. L'eau utilisée contient toujours, en pratique, quelles que soient les précautions prises, un peu de  $\text{CO}_2$  dissous ( $\text{pH} < 7$ ). Dans la méthode officielle, l'introduction de cette eau, juste avant le titre final, entraîne une erreur positive sur le résultat. En effet, l'acidité de ce  $\text{CO}_2$  qui s'ajoute à celle des acides faibles présents dans les préparations, est titrée jusqu'à  $\text{pH}$  8,1, dans le cas du dosage, mais pas dans le cas de l'essai à blanc, arrêté au  $\text{pH}$  6,5. Par contre, dans la méthode modifiée, où la dilution est effectuée avant la mise au  $\text{pH}$  de départ, cette acidité est neutralisée avant de commencer les opérations, supprimant ainsi toute possibilité d'erreur.

Cet effet secondaire peut être mis en évidence, d'une façon très simple, par un essai comparatif au cours duquel des préparations identiques sont traitées par la méthode officielle ou par la méthode modifiée comportant la dilution préalable. Les titrages sont arrêtés dans tous les cas, pour uniformiser les conditions de traitement, au point d'inflexion des courbes de titrage, tracées manuellement avec précision.

Un tel essai nous a donné les résultats suivants.

Méthode	Essai à blanc, <i>ml</i>	Dosage, <i>ml</i>
Officielle	4,910	29,890
	4,910	29,900
Modifiée	4,880	29,880
	4,870	29,870
Différence	0,035	0,020

La différence des essais à blanc représente, exprimée en glycérol, une erreur positive de 0,14% due à l'apport de  $\text{CO}_2$  par l (eau de dilution). La différence des titres de dosage résulte, à la fois, de l'apport de  $\text{CO}_2$  par l'eau de dilution et du départ d'acide formique dans la méthode officielle. Le gain de titre,  $0,035 - 0,020 = 0,015$  ml, imputable à la dilution préalable, équivaut à une perte d'acide formique dans la méthode officielle de 0,06% du titre en glycérol.

Les données fournies par un essai comparatif du même type que le précédent permet d'étayer statistiquement cette conclusion. Il a été réalisé, cette fois, en prenant des précautions particulières pour supprimer toute trace de  $\text{CO}_2$  dans l'eau utilisée pour les dilutions. En voici les résultats moyens calculés sur 13 répétitions de la comparaison.

Méthode	Officielle			Modifiée		
	Dosage	Blanc	Net	Dosage	Blanc	Net
Titres moyens, <i>ml</i>	42,025	4,569	37,456	42,057	4,561	37,496
Répétabilité, <i>ml</i> pour $P = 95\%$	$\pm 0,041$	$\pm 0,022$	$\pm 0,043$	$\pm 0,037$	$\pm 0,041$	$\pm 0,034$

L'analyse statistique de ces résultats montre que la différence entre les essais à blanc ( $-0,008$  ml) n'est pas significative. Le  $\text{CO}_2$  apporté par l'eau de dilution a donc bien été négligeable dans l'expérience considérée.

Par contre, la différence entre les titres des dosages ( $+0,032$  ml) et celle entre les titres nets ( $+0,040$  ml) sont hautement significatives ( $P > 99\%$ ). La seconde qui représente la diminution de la perte d'acide formique, équivaut à un gain de titre en glycérol de  $0,1\%$  environ, imputable à la dilution préalable.

### *Le choix du point final des titrages*

Dans la méthode officielle, l'arrêt du titre de l'essai à blanc au pH 6,5 masque le phénomène compensatoire défini plus haut. Ce choix empirique du point final perd toute justification dès l'instant où ces erreurs systématiques et le moyen de les supprimer sont connus car elles sont également sources d'erreurs accidentelles et ne peuvent, a priori, que diminuer la reproductibilité.

Il est apparu, au cours des nombreux essais effectués depuis notre première publication, que les points d'inflexion, déterminés dans le cas des courbes de titrage des essais à blanc, présentent des variations (entre 6,8 et 7,65) telles que le choix d'un pH défini comme point final semble illusoire. Nous avons constaté, en outre, dans la pratique courante, que l'arrêt au pH  $6,5 \pm 0,1$ , prescrit par la méthode officielle, est rarement respecté. La dernière goutte de solution titrante provoque généralement un saut de pH supérieur à une unité. Certains opérateurs la déduisent du volume utilisé, ce qui augmente le titre net en glycérol. D'autres comptent dans le titre la goutte qui fait dépasser le pH prescrit, d'où manque de reproductibilité.

Devant cette situation, l'un de nous (E.H.) a proposé d'ajouter aux préparations un peu d'ions formiques avant le titre final. Cet apport a deux effets heureux. D'une part, il permet d'uniformiser la place du point d'inflexion de l'essai à blanc et du dosage. On a déterminé que la présence d'au moins 5 milliéquivalents de formiate de sodium dans les préparations stabilise le point d'inflexion à pH  $7,87 \pm 0,13$ . D'autre part, l'effet tampon de ce formiate modifie et régularise la courbe de titrage de l'essai à blanc ce qui améliore nettement la reproductibilité et, en principe, l'exactitude de la méthode. Le diagramme de la fig. 2 montre bien l'amélioration intervenue dans ce domaine.

### *Conclusions*

De l'ensemble des éléments présentés dans nos deux communications, il apparaît que la méthode établie primitivement par l'American Oil Chemists Society<sup>3,4</sup> sur la base des travaux de Malaprade<sup>5</sup> présente un certain empirisme, nécessaire pour en faire coïncider les résultats avec ceux de la méthode densimétrique<sup>6</sup> et caractérisé par la dualité des pH de fin de titrage.

Nos travaux ont montré que ce choix empirique, et la coïncidence de résultats qui en découle, ne sont en fait justifiés que par le jeu d'erreurs systématiques compensatoires dont les effets peuvent être largement atténués par l'adoption de modifications de détail du mode opératoire.

Ainsi modifié, celui-ci devient parfaitement orthodoxe puisqu'il rétablit le principe même de *l'essai à blanc réel*, indispensable à la correction automatique des erreurs accidentelles et à l'obtention des valeurs reproductibles.

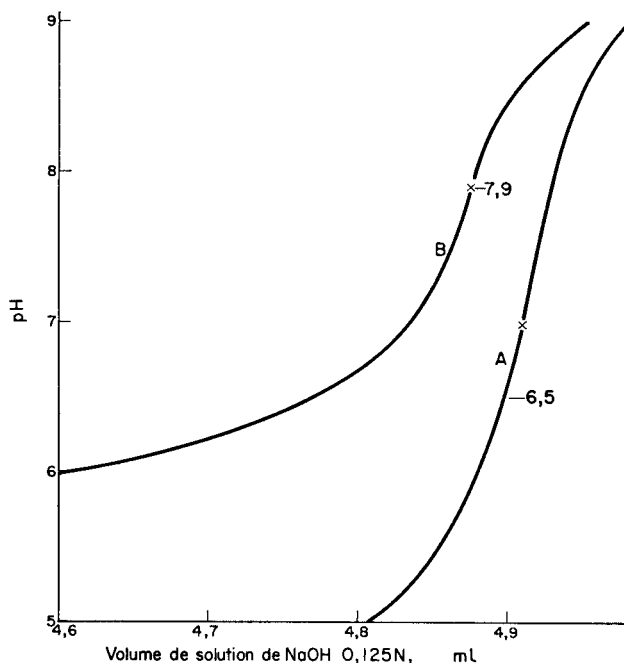


FIG. 2.—Courbes de titrage potentiométrique de l'essai à blanc.

A: Méthode officielle U.I.C.P.A.

B: Méthode modifiée par l'addition de formiate de sodium

×: Point d'inflexion

←: Point final prescrit

Afin de permettre aux laboratoires intéressés de vérifier, dans la pratique courante, le bien-fondé de ces conclusions, nous donnons, ci-après, quelques détails sur le mode opératoire recommandé, espérant avoir ainsi contribué à l'établissement d'une méthode parfaitement définie dont l'adoption faciliterait grandement les transactions internationales.

## PARTIE EXPÉRIMENTALE

### Réactifs

Tous les réactifs utilisés dans la méthode officielle<sup>2</sup> ont été conservés à l'exception de l'hydrogénophthalate de potassium, étalon primaire servant au calibrage de la solution titrée d'hydroxyde de sodium. On s'est aperçu en effet, au cours d'un vaste essai comparatif groupant 18 laboratoires répartis dans 6 pays, que ce produit présente de lot à lot des variations des teneurs telles que la reproductibilité de la méthode en est affectée de façon très sensible. On lui a substitué ici, comme étalon d'acidimétrie, le carbonate de sodium obtenu par surséchage du sesquicarbonate de sodium, préparé conformément aux recommandations de la Society for Analytical Chemistry.<sup>7</sup>

On a, en outre, utilisé une solution env. *N* de formiate de sodium.

### Mode opératoire recommandé

Diluer la prise d'essai qui ne peut contenir plus de 0,50 g de glycérol, jusqu'au volume de 250 ml environ, au moyen d'eau pure récemment bouillie et refroidie. Neutraliser par l'hydroxyde de sodium (env. 0,05*N*) jusqu'au pH  $7,9 \pm 0,1$  vérifié au pH-mètre.

Ajouter 50,0 ml de solution de métaperiodate de sodium (60 g/l dans H<sub>2</sub>SO<sub>4</sub> env. 0,012*N*). Couvrir la préparation et laisser reposer pendant 30 min à l'obscurité dans un endroit frais.

Ajouter alors 10 ml de solution aqueuse à 50% de 1,2 éthanediol. Homogénéiser et laisser reposer encore pendant 20 min dans les mêmes conditions.



Ajouter enfin 5 ml de solution env.  $N$  de formiate de sodium et titrer l'acidité au moyen d'hydroxyde de sodium 0,125 $N$  jusqu'au pH  $7,9 \pm 0,2$  vérifié au pH-mètre. (L'utilisation d'un indicateur, le rouge de phénol par exemple, est possible dans le cas des glycélines peu colorées moyennant l'emploi d'une solution de comparaison, tamponnée au pH voulu.)

Effectuer, de façon identique et parallèlement au dosage, un essai à blanc comportant tous les réactifs à l'exception de la prise d'essai et dont le titre sera déduit de celui du dosage pour le calcul de l'acidité formique équivalente au glycérol présent dans la prise d'essai.

**Summary**—The authors confirm experimentally the hypothesis of the volatilization of formic acid during the volumetric determination of glycerol by the periodate method. The reproducibility of the results can be improved if sodium formate is added.

**Zusammenfassung**—Die Autoren liefern einen experimentellen Beweis für die Hypothese, daß bei der volumetrischen Bestimmung von Glycerin mit der Perjodatmethode Ameisensäure flüchtig geht. Durch Zusatz von Natriumformiat kann die Reproduzierbarkeit der Ergebnisse verbessert werden.

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## OXYGEN DETERMINATIONS WITH THE ALUMINIUM CORROSION ELECTRODE

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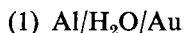
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**Summary**—A method for the determination of molecular oxygen in a great variety of liquid and gaseous samples has been developed. The method seems adaptable for control analysis by reason of its sensitivity, rapidity and ease of operation. It gives accurate determinations in the presence of many chemical substances which interfere with other methods. It is based on the variation in corrosion potential of the aluminium electrode, caused by oxygen, and exemplifies use of the corrosion phenomenon in analytical chemistry.

ONE of us has shown the high sensitivity of the aluminium corrosion electrode to molecular oxygen.<sup>1,2</sup> Later this property was used for analytical purposes.<sup>3,4</sup> These preliminary results have shown the possibility of developing an analytical method which is accurate, sensitive, specific, versatile, and fast; the present paper describes the realization of a method for determination of 0.3–8  $\mu\text{g}$  of oxygen in 0.1–1 ml of liquid, in 4–6 min, or 4–60 ng of oxygen in 0.01–3 ml of gas, in 20 sec.

The determinations are based on the transient variation of the e.m.f.,  $E$ , of the cell:



which occurs when the oxygen of the sample, carried by an inert gas, is introduced for a short time into the cell (1). In the cell (1) the gold electrode behaves as a quasi-reference electrode; the variation in  $E$  is due to the variation of the corrosion potential of the aluminium electrode.

### EXPERIMENTAL

The aluminium electrodes are made with 99.5% pure wire 1-mm thick, the gold electrodes with pure metal wire 1-mm thick. It has been shown that the purity of the aluminium does not affect electrode performance provided an aluminium oxide covers the electrode surface.<sup>1–4</sup> The gold electrode is insensitive to oxygen.<sup>5</sup> Experiments made with the cell  $\text{Au}/\text{H}_2\text{O}/\text{S.C.E.}$  have confirmed its insensitivity to oxygen at any level of concentration and have shown that the potential of the gold electrode in water becomes stable in a short time, if it has not been treated drastically.

The analysis cells are shown in Fig. 1 (for liquid samples) and in Fig. 2 (for gaseous samples). In the analysis cells the aluminium electrode tip is wet by water held by a rigid support (sintered-glass disk, cell 1) or a soft support (cotton thread, cell 2). This allows a rapid exchange of oxygen between the gaseous and liquid phases, but does not clearly define the active wet part of the aluminium electrode. A well defined electrode area is not necessary, but the wet area must not vary during an experiment, because that would cause variation in  $E$ . In practice this risk is limited, and naked aluminium electrodes can be used.

Before use, the aluminium wire is cleaned with diethyl ether and cotton wool, then with distilled water, and is dried with filter paper; then its tip is cut with well-cleaned steel pliers, immediately before it is introduced into the cell. The gold wire is cleaned with distilled water and filter paper.

Before each experiment, the analysis cells must be soaked in cold chromic acid cleaning mixture for at least 30 min and then rinsed carefully with distilled water. If the cleaning is omitted, or not done carefully, or done too soon, the experiment will be profoundly affected. It must be emphasized

that all precautions should be taken regarding general cleaning during the assembling of the analysis cell.

First the apparatus is deoxygenated with cylinder hydrogen or nitrogen purified by passage through kieselguhr containing 10–15% copper, at 250–270°. The oxygen content of the carrier gas is  $<10^{-4}\%$ .<sup>8</sup> The flow-rate of the carrier gas must be kept constant during a set of determinations; its value is 1–2 ml/sec and is measured with a soap-bubble flow-meter and controlled by a rotameter.

After deoxygenation of the apparatus, the analysis cell is assembled. Initially,  $E$  of the cell (1) is rather variable, but in 1–2 hr, the cell and the water contained in it become deoxygenated and the electrode potential reaches a nearly steady state, and its drift is small ( $<1$  mV/min, Fig. 3); determinations can then be started. For this purpose the oxygen of the sample or of the standard is introduced into the carrier-gas stream. With liquid samples it is the carrier gas itself which extracts the oxygen from the sample, introduced into an appropriate cell (Fig. 4). With gaseous samples, a

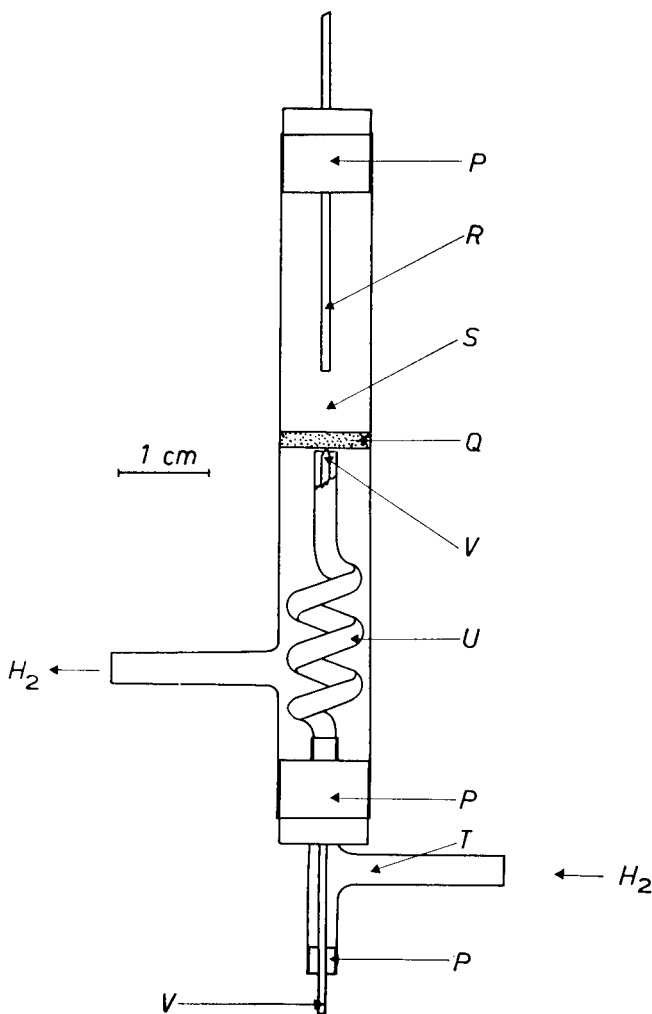


FIG. 1.—Analysis cell for liquid samples.

(P) Rubber stoppers; (Q) sintered-glass disk, porosity 4; (R) Au electrode; (S) distilled water; (T) glass tube; (U) Tygon tube, o.d. 4 mm, bore 2 mm; (V) Al electrode. The cell is placed at an angle of 45° with the Al electrode down. The coiled arrangement of the aluminium wire and of the Tygon tube make a light but sure contact of aluminium with the sintered-glass disk.

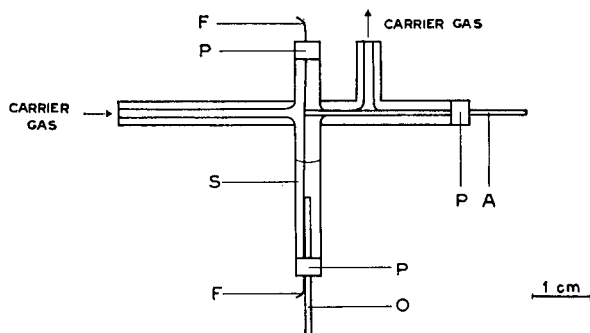


FIG. 2.—Analysis cell for gaseous samples.

(A) Al electrode; (O) Au electrode; (F) cotton thread; (S) distilled water; (P) Tygon stoppers.

small volume of standard or sample gas is introduced into the carrier-gas stream with the help of a glass loop (see Fig. 6). The volume of the loop is measured by weighing the amount of mercury it will hold; the volume of the loop used is based on the oxygen content of the sample.

In the analysis cell, three processes occur: part of oxygen passes from the gaseous phase to the liquid one; part of the dissolved oxygen diffuses to the tip of the aluminium electrode, where it is consumed, determining the  $E$  variation; the oxygen which has not reacted diffuses far or is eliminated in a short time. After the oxygen elimination,  $E$  reverts to its initial value or to one very close.

The tubing must be of uniform small diameter, to minimize mixing and dilution of sample with carrier gas. Tygon tubing can be used with high concentrations of oxygen, but for very low concentrations ( $10^{-2}$ – $10^{-4}$ %), glass or metal tubing and gas-tight junctions must be used.

The apparatus for analysis of liquid samples is shown in Fig. 5. The determinations can be carried out over a long period (at least 10 hr) starting from when the drift in  $E$  is sufficiently low (1–2 hr after assembly of the cell). The volume of the liquid in the stripping cell  $D$  is kept constant (2 ml); carrier gas is passed along path 1–2, a volume of liquid (0.1–1 ml) is drawn off from the stripping cell, and an equal volume of sample or standard liquid is introduced. Immediately afterwards, the carrier gas is passed along path 1–3–4 and the variation in  $E$  is recorded or  $\Delta E_{\max}$  is directly measured.

The apparatus for gaseous samples is shown in Fig. 6. The determination can be carried out over a period of at least 10 hr from when the drift in  $E$  is sufficiently low (30–60 min after assembly of the cell). Known volumes of standard or sample are introduced by means of the loops. The standards

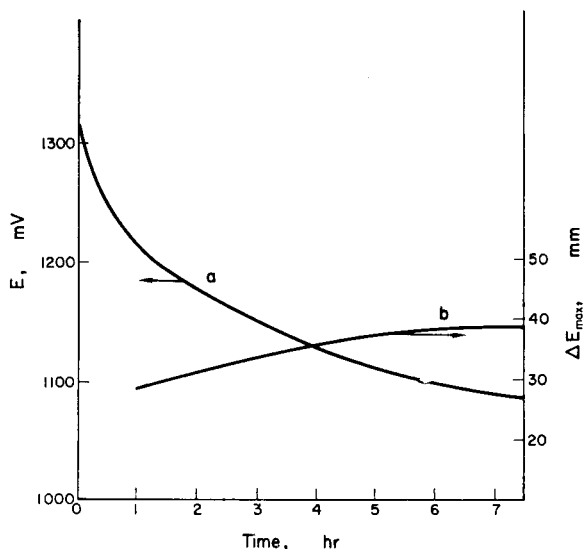


FIG. 3.—Typical behaviour of the e.m.f. of the Al/H<sub>2</sub>O/Au cell and of its sensitivity to O<sub>2</sub> with time, with gaseous samples.

(a)  $E$ ; (b) sensitivity ( $\Delta E_{\max}$  in mm, relative to 20 ng of O<sub>2</sub>).

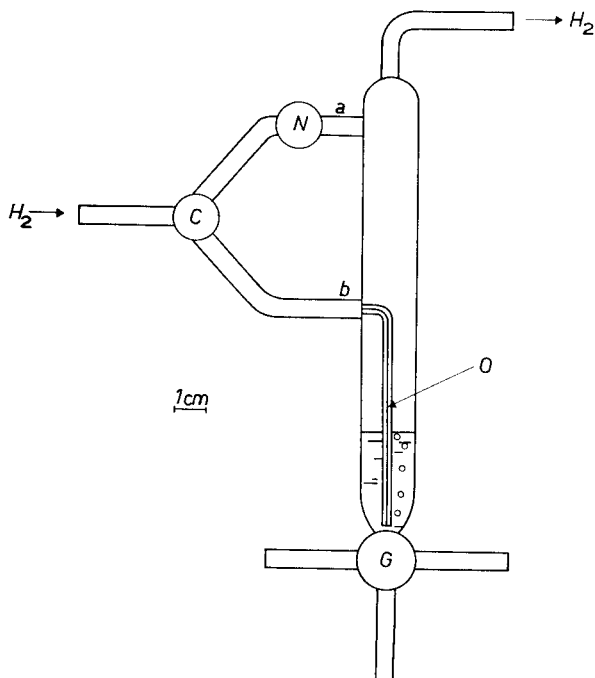


FIG. 4.—Stripping cell.

(C) Two-way stop-cock; (G) three-way stop-cock; (N) stop-cock to make the gas flow-rate the same through *a* and *b*; (O) tube for introducing carrier gas, bore 0.2–0.3 mm.

are prepared by coulometrically generating oxygen in a cell (Fig. 7) through which an inert gas passes at an accurately known rate. As inert gas for the standard we used 99.999% pure nitrogen for analysis of samples containing from 0.6 to 0.03% oxygen, and nitrogen purified by passage over catalytic copper at 250° for samples with lower oxygen content. The time for a determination is 20 sec, but the cell (1) responds to oxygen in about 3 sec.

To measure  $\Delta E_{\max}$ , various electrical devices can be used, but a high input impedance is necessary because of the high polarizability of the cell (1).

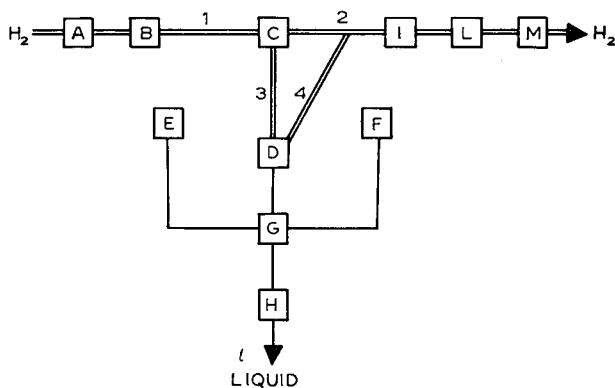


FIG. 5.—Diagram of apparatus for analysis of liquid samples.

(A) Furnace for purifying carrier gas; (B) wash-bottle; (C) two-way stop-cock; (D) stripping cell (Fig. 4); (E and F) containers of sample and standard liquids (10-ml burettes graduated to 0.02 ml); (G) three-way stop-cock; (H) graduated pipette for measuring volume of discarded liquid; (I) analysis cell (Fig. 1); (L) drying tube with silica gel; (M) flow-meter.

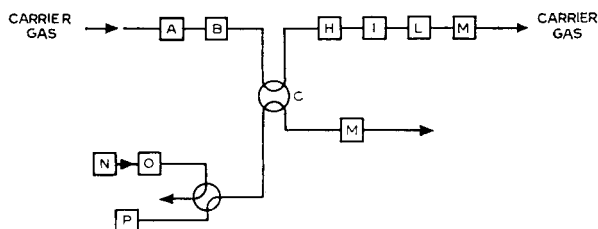


FIG. 6.—Diagram of apparatus for analysis of gaseous samples.

(A) Furnace for purifying carrier gas; (B) humidifier; (H) trap for interfering gaseous chemical substances; (I) analysis cell (Fig. 2); (L) drying tube; (M) flow-meters; (N) gas for the preparation of the standard; (O) cell for electrolytic generation of  $O_2$  (Fig. 7); (P) gaseous sample; (C) sampling loop of gas-chromatographic on-line sampling type.

For liquid samples, when the variation in  $E$  is sufficiently slow, a pH meter can be used to measure  $\Delta E_{\max}$  directly. With gaseous samples, variation in  $E$  is very rapid, and it is necessary to couple the pH meter with a recorder. We used a Beckman 1019 meter and either a Bausch and Lomb VOM 6 recorder or a Sargent MR with a  $500\text{-}\Omega$  resistance interposed.

For the coulometric generation of oxygen we used a Sargent coulometric source for  $10^{-2}$ – $1\%$  oxygen, and for lower concentrations a system comprising a Trygon Electronics Inc. power supply model RS 320, 1.2 BE, two resistances in series to the cell (one of  $100\text{ k}\Omega$  and the other of  $1\text{ k}\Omega$ , the latter for measuring the current by means of a Beckman GS pH meter). The oxygen content of the gas coming from the coulometric cell is calculated from the formula  $[O_2] = 16.14(i T)/(Fp)$  where  $i$  is the current in A,  $T^\circ$  is the temperature,  $F$  is the carrier gas flow rate in ml/sec and  $p$  is its pressure in mmHg.

The analysis cells must be well dried externally, electrically insulated and possibly shielded. Measurements are disturbed by stray currents (the effect of which is only temporary) and by polarization (the effect of which is permanent); however they tolerate mechanical vibrations and shocks well, except for violent shocks capable of altering the position or the wetting of the tip of the aluminium electrode.

## RESULTS

The quantity measured for analytical purposes is the maximum variation of  $E$  following the introduction of oxygen into the cell (1). The relationship between

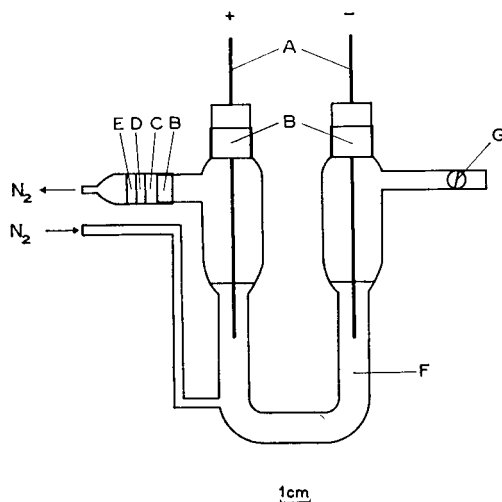


FIG. 7.—Coulometric cell for oxygen generation.

(A) Pt electrodes; (B) ground-glass joints; (C) cotton wool; (D)  $KHSO_4$  crystals; (E) sintered-glass disk,  $G_2$ ; (F)  $1M$  NaOH, 1 ml; (G) stop-cock. The cell is preliminarily deoxygenated in both compartments; during the generation of  $O_2$  the stop-cock (G) is closed.

$\Delta E_{\max}$  and  $[O_2]$  is the simplest possible:  $\Delta E_{\max} = K[O_2]$ . The constant  $K$  is generally different for each experiment and is calculated from a standardization.  $K$  varies with time (Fig. 3) but so slowly (especially after some hours of experiment) that it is valid for several determinations. The necessity of repeated standardizations is not a serious inconvenience, because of the rapidity of execution.

In Tables I, II and III the limits of validity of the formula for  $\Delta E_{\max}$  are reported

TABLE I.—RELATIONSHIP BETWEEN  $[O_2]$  AND  $\Delta E_{\max}$  FOR LIQUID SAMPLES

$v$ <i>ml</i>	$[O_2]$ $10^{-4}M$	$\Delta E_{\max}$ <i>mV</i>	$K$ $10^4 \text{ mV.l/mole}$
0.70	1.00	17.8	18.0
0.70	1.00	18.2	18.0
0.70	1.00	18.3	18.5
0.80	1.15	21.2	18.5
0.80	1.15	21.3	18.5
1.00	1.43	25.8	18.0
1.00	1.43	26.5	18.5
1.00	1.43	26.6	18.5
1.00	1.43	26.5	18.5
1.00	1.43	26.4	18.5
0.40	0.57	23.1	40.5
0.40	0.57	24.3	42.5
0.50	0.71	30.1	42.5
0.50	0.71	30.9	43.5
0.50	0.71	30.3	42.5
0.60	0.85	36.4	43.0
0.60	0.85	35.8	42.0
0.40	0.57	24.3	42.5
0.40	0.57	24.0	42.0
0.40	0.57	24.4	43.0
0.50	0.71	29.9	42.0
0.50	0.71	30.1	42.5
0.50	0.71	29.3	41.5
0.50	0.71	30.2	42.5

Temperature = 20°C; carrier gas flow = 1 ml/sec; volume of liquid in the stripping cell = 2 ml;  $v$  = added volume of aerated water;  $[O_2]$  in aerated water at 20°C =  $2.86 \times 10^{-4}M$ ; determinations made after 4–5 hr from the beginning of the experiment; results of two different experiments.

for both analysis cells. For the gas-cell, in a series of measurements (20 at the beginning of each 30 min, 10 for each route of the loop, each series lasting  $\sim 8$  min, total run 7 hr 30 min) the relative standard deviation of  $\Delta E_{\max}$  for each set of 10 measurements ranged from 1.5 to 6%.

In Table IV the results of analysis of liquid samples are compared, when possible, with values obtained by other authors. In the case of formamide, we used a trap (a simple glass tube filled with potassium hydrogen sulphate crystals) for the ammonia extracted from the liquid together with the oxygen, which would otherwise interfere with the results because it causes variations in  $E$ . In Table V the results of analysis of gaseous samples are given.

TABLE II.—RELATIONSHIP BETWEEN  $[O_2]$  AND  $\Delta E_{\max}$  FOR GASEOUS SAMPLES WITH  $O_2$  CONCENTRATION FROM 0.03 TO 0.6% v/v

Duration of experiment <i>min</i>	$[O_2]$ , %	$\Delta E_{\max}$ , <i>mm</i>		$K$ , <i>mm</i> /%	
70	0.030	5.5	5.5	185	185
	0.0605	12.0	12.5	200	205
	0.121	26.0	26.5	215	220
	0.302	64.0	65.0	210	215
90	0.044	8.5	9.0	195	205
	0.087	17.5	18.5	200	210
	0.175	36.0	36.0	205	205
	0.440	90.0	94.0	205	215
105	0.061	12.5	12.5	205	205
	0.122	25.5	25.5	210	210
	0.245	50.0	51.0	205	210
	0.610	122.5	122.0	200	200
115	0.072	14.5	14.5	200	200
	0.145	28.5	29.5	200	205
	0.290	59.5	61.0	205	210
125	0.086	18.0	18.0	210	210
	0.173	36.5	36.0	210	210
	0.346	72.0	72.0	210	210

Carrier gas: purified  $H_2$ , 1 ml/sec; gas for the standard:  $N_2$ , 99.999% pure, 0.3–1 ml/sec; loop 1, volumes of the two routes 0.033 and 0.034 ml; recording with VOM-6 (1 mV = 7 mm). At each value of  $[O_2]$  8 determinations were made, 4 for each route of the loop. For each series of determinations, the  $N_2$  flow was constant; the variation of  $[O_2]$  was obtained rapidly by varying the electrolysis current of the coulometric cell.

#### DISCUSSION

Every variation in e.m.f. of the cell (1), in our experimental conditions, is due to the aluminium electrode. This is a corrosion electrode<sup>2</sup> which, in the described experimental conditions (electrode in a liquid which does not dissolve the surface oxide film; absence of agents, e.g., oxygen, promoting growth of surface oxide film; no mechanical rupture of oxide film) is covered by a hydrated oxide film which grows increasingly slowly due to the stifling effect on corrosion rate. In the absence of oxygen, growth of the film determines the rise of anodic polarization, a positive change in the potential of the aluminum electrode and a slower and slower decrease in  $E$ . The drift in  $E$  from that time on becomes so low that it does not affect the determinations: for practical purposes, we can speak of a steady state. At this point, the oxygen introduced depolarizes the cathode locally, giving a net increase in the corrosion current, a positive change in the aluminum potential and a decrease in  $E$ ; but obviously also causes a more rapid growth of the film, thus altering the electrode state. If, however, oxygen is introduced into the cell for a short time and in a small quantity, its permanent effect is limited,  $E$  reverts to its initial value or to one very close, and thus the sensitivity to oxygen remains the same.

The influence of stray currents is due to electrode state variations, which are small but can disturb measurements. Polarizations, on the other hand, can change the state of the cell (1) profoundly. In any case, in the course of an experiment, if the cause of polarization is eliminated, the determinations can be continued, beginning from new values of  $E$  and of oxygen-sensitivity, pertaining to the new electrode state.



TABLE III—RELATIONSHIP BETWEEN  $[O_2]$  AND  $\Delta E_{\max}$  FOR GASEOUS SAMPLES WITH OXYGEN CONCENTRATION *A*  $1-4 \times 10^{-3}\%$  v/v, *B*  $2.5-15 \times 10^{-4}\%$  v/v

	$[O_2]$ , $10^{-3}\%$	$\Delta E_{\max}$ , <i>mm</i>	<i>K</i> <i>mm/</i> %
<i>A</i>	1.03	18.5	18.0
	2.06	37.5	18.0
	3.09	58.0	18.5
	4.12	74.5	18.0
	1.03	18.0	17.5
	2.06	37.5	18.0
	3.09	55.0	18.0
	4.12	72.0	17.5
	1.03	17.0	16.5
	2.06	36.5	17.5
	3.09	57.0	18.5
	4.12	75.5	18.5
	1.03	18.0	17.5
	2.06	38.0	18.5
	3.09	52.0	17.0
	4.12	72.0	17.5
<i>B</i>	1.03	17.0	16.5
	2.06	36.0	17.5
	3.09	58.0	18.5
	4.12	74.0	18.0
	0.25	7.0	28.0
	0.50	12.0	24.0
	1.00	23.0	23.0
	1.50	35.5	23.5
	0.25	7.5	30.0
	0.50	12.0	24.0
1.00	24.5	24.5	
1.50	37.5	25.0	

Carrier gas: purified  $N_2$ , 0.5 ml/sec; gas for the standard: purified  $N_2$ , 1 ml/sec; *A* 0.5-ml loop; *B* 3-ml loop; recording with VOM-6: (1 mV = 15 mm). At each value of  $[O_2]$ , 4 determinations were made. The flow of  $N_2$  was constant and the variation of  $[O_2]$  in the standard gas was obtained by varying the electrolysis current of the coulometric cell.

The same holds for shocks capable of scratching the electrode surface or of changing its wetting state.

The sensitivity to oxygen, expressed as minimum detectable concentration, depends, without doubt, on the state of the aluminium electrode, but essentially on the degree of deoxygenation of the carrier gas and of the electrode liquid. The latter, in our experimental conditions, does not have to be very low, because the cells employed are not completely gas-tight and are liable to air-contamination, and probably this is the limiting factor at the present state of the research.

The sensitivity, expressed as an absolute quantity of oxygen, depends essentially on the geometry of the cell, that is, on the fraction of the oxygen in the sample which succeeds in reaching the aluminium electrode tip and in reacting with it; this fraction is certainly not increased with the described cells.

TABLE IV.—RESULTS OF ANALYSIS OF LIQUID SAMPLES

Sample	No. of determinations*	[O <sub>2</sub> ] found, † 10 <sup>-4</sup> M	[O <sub>2</sub> ] (literature value) 10 <sup>-4</sup> M	Temp., °C	Reference
1M KOH	12	2.10		18	
	10	2.00		20	
			2.01	15	7
			1.93	20	9
			1.72	25	8
			1.77	25	7
1M NaOH	16	1.75		22	
	16	1.60		23	
	10	1.70		23	
	16	1.70		23	
	12	1.75		23	
	15	1.65		24	
			1.99	15	7
		1.75	25	7	
1M NaCl	5	2.10		19	
	4	2.15		19	
	6	2.05		20	
			2.25	15	7
			1.91	25	7
1M H <sub>2</sub> SO <sub>4</sub>	17	2.55		14	
	12	2.30		19	
			2.70	15	7
			2.05	25	7
			1.86	25	8
1M K <sub>2</sub> CrO <sub>4</sub>	16	1.15		23	
	13	1.10		24	
	18	1.15		24	
	16	1.10		25	
	Dimethylsulphoxide	14	4.65		19
9		4.75		19	
8		4.65		20	
			4.20	25	10
Formamide	12	2.85		19	
	12	2.75		22	
			2.85	19	11

\* Relative standard deviation, for each group of determinations, ranges from 0.7 to 3%.

† Values referred to the indicated temperature, 1 atm pressure, and standard distilled water.<sup>12</sup>

### CONCLUSIONS

The use of the aluminium corrosion electrode for oxygen determination is based on the possibility of reaching an almost steady electrode state, the high sensitivity of the aluminium electrode to oxygen, the very rapid reaction with oxygen, the limited alteration of the electrode state, provided that the oxygen is in contact for a short time and in small quantity, the linear relationship between [O<sub>2</sub>] and  $\Delta E_{\max}$ .

Because the aluminum electrode is sensitive to numerous chemical substances,\* it may in the future be utilized for other substances than oxygen. This sensitivity

\**E.g.*, formic acid, acetic acid, metal ions,<sup>2</sup> substances varying the pH,<sup>24,25</sup> oxidants, corrosion inhibitors and accelerators.

TABLE V.—RESULTS OF ANALYSIS OF GASEOUS SAMPLES

Sample	No. of determinations of $K$ and of $[O_2]$	$K$ , $mm/\%$	$[O_2]$ found %
Tank $H_2$	4	335	0.083
	4	325	0.082
	3	335	0.082
	1	330	0.083
	5	340	0.082
Tank $N_2$ (I)	2	117	0.57
	5	118	0.57
	6	94	0.56
	1	102	0.58
Tank $N_2$ (II)	2	145	0.72
	4	78	0.76

creates, however, problems of interference, as in the case of ammonia in the determination of oxygen in formamide, but the use of traps may widely extend the application of the method.

The sensitivity might be increased by improving the apparatus and the geometry of the analysis cell, and by reducing the shift and noise of  $E$ . Some factors to be considered for this purpose are the rate and area of impact of the carrier gas, the screen effect exercised by aluminium wire and cotton thread, better and faster deoxygenation of the analysis cell, gas-tightness of the cell to atmospheric oxygen and elimination of noise due to stray currents.

The performance of the method may be compared with that of the two most modern instrumental analytical methods for the determination of oxygen, (a) that using a galvanic or electrolytic cell with or without membrane protection, and (b) the gas chromatographic method. The comparison (Table VI) is limited to analysis of samples with low oxygen concentration.

For liquid samples the proposed method has the following advantages over method (a): possibility of eliminating interfering gases dissolved in the sample; analysis of non-aqueous liquids or liquid samples containing interfering substances

TABLE VI.—COMPARISON WITH OTHER RECENT METHODS OF  $O_2$  DETERMINATION

Method	$[O_2]$ ,	Sample size, $ml$	Limit of detection	Duration of analysis	References
<i>Liquid samples</i>					
Galvanic or voltammetric cell with membrane	$10^{-5}$ – $10^{-3}M$		$10^{-6}M$	few sec	13–15
Gas chromatography	$10^{-5}$ – $10^{-4}M$	0.5–2	$2 \times 10^{-6}M$	10–20 min	16–18
Al electrode	$10^{-5}$ – $10^{-3}M$	0.1–1	$10^{-6}M$	4–6 min	
<i>Gaseous samples</i>					
Galvanic or voltammetric cell without membrane	$10^{-4}$ –0.1%	2	$10^{-4}\%$	15 min	19
Gas chromatography	$2 \times 10^{-3}$ –0.1%	1	$2 \times 10^{-3}\%$	6 min	20–22
Al electrode	$10^{-4}$ –1%	$10^{-2}$ –3	$10^{-4}\%$	20 sec	

(apart from those already mentioned), such as physiological products, bacteria cultures or suspended matter, which can affect the permeability of the membrane, causing the cell to be inoperative. For gas samples the method has the advantage of rapidity.

The advantages over method (b) are rapidity, simplicity and low cost, and insensitivity of the aluminium electrode to inert gases such as nitrogen, argon, hydrogen. However, the recent helium detector<sup>23</sup> should allow a higher sensitivity than that so far obtained with our method.

*Acknowledgement*—Financial aid received from the Consiglio Nazionale delle Ricerche is gratefully acknowledged.

**Résumé**—On a élaboré une méthode pour le dosage de l'oxygène moléculaire dans une grande variété d'échantillons liquides et gazeux. La méthode semble adaptable à l'analyse de contrôle en raison de ses sensibilité, rapidité et facilité d'opération. Elle donne des déterminations précises en la présence de nombreuses substances chimiques qui interfèrent dans d'autres méthodes. Elle est basée sur la variation de potentiel de corrosion de l'électrode d'aluminium, causée par l'oxygène, et illustre l'emploi du phénomène de corrosion en analyse chimique.

**Zusammenfassung**—Eine Methode zur Bestimmung von molekularem Sauerstoff in einer großen Menge flüssiger und gasförmiger Proben wurde entwickelt. Es scheint, daß sich das Verfahren wegen seiner Empfindlichkeit, Schnelligkeit und leichten Ausführung für die Regelungsanalyse anpassen läßt. Es liefert genaue Werte in Gegenwart vieler Chemikalien, die bei anderen Methoden stören. Es beruht auf der durch Sauerstoff verursachten Änderung der Korrosionsspannung der Aluminiumelektrode und stellt ein Beispiel für den Gebrauch von Korrosionserscheinungen in der analytischen Chemie.

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## ANALYTICAL ASPECTS OF ORGANO-P, As, Sb, S, Se, Te AND Sn(IV) (ONIUM) CATIONS

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**Summary**—Reactions and the analytical applications of tetraphenylphosphonium, -arsonium and -stibonium, triphenylmethylarsonium, triphenyl-sulphonium, -selenonium and -telluronium and triphenyltin cations with oxy-anions, and halo- and thiocyanato-anionic complexes are surveyed.

THE ammonium salts are the best known representatives of a large class of compounds with the following characteristics. The positive ion consists of a central atom of an element from the nitrogen, oxygen or halogen groups, surrounded by from two to four hydrogen atoms or organic radicals. All these onium ions, as they are frequently termed, have a single positive charge and are of extreme interest as precipitants and extractants in analytical chemistry.

The preparations and general properties of onium compounds have been reviewed by Heal.<sup>1</sup> Detailed accounts of the preparation of the multivalent iodine compounds have been given by Sandin<sup>2</sup> and Banks.<sup>3</sup> The heterolytic decomposition of diphenyl-halogenonium and triphenyloxonium salts has been surveyed by Nesmeyanov *et al.*,<sup>4</sup> who, in addition, give further details of stable chloronium and bromonium salts first reported by Sandin and Hay.<sup>5</sup>

Analytical applications of the tetraphenylarsonium ion have been studied in great detail and these applications, together with those of the less well known onium ions, are considered in this review. The extensive analytical applications of the quaternary ammonium salts have been omitted for conciseness.

### REVIEW OF REACTIONS

#### *Reactions of the tetraphenylarsonium cation*

*Tetraphenylarsonium chloride.* This was first proposed as a reagent in 1939 by Willard and Smith<sup>6</sup> for the determination of mercury(II), tin(IV), cadmium, zinc, perrhenate, periodate and perchlorate. Three types of reaction were noted in which the reagent was useful.

(a) The formation of insoluble salts by the combination of the tetraphenylarsonium ion with oxy-anions such as perrhenate, permanganate, periodate and perchlorate.

(b) The formation of insoluble compounds by the combination of the tetraphenylarsonium ion with halide complexes of mercury(II), tin(IV), cadmium, and zinc.

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(c) The formation of insoluble compounds with thiocyanato-complexes such as those of iron and cobalt.

Many of these reactions have since been examined in detail and shown to be the basis of useful determinations.

(a) The formation of white crystalline water-insoluble tetraphenylarsonium perrhenate<sup>7</sup> permits the gravimetric, or, if excess of reagent is titrated with iodine, the titrimetric determination of perrhenate. Only those ions which form insoluble tetraphenylarsonium salts, as outlined earlier, interfere. Metavanadate does not interfere, and the precipitation of molybdate is hindered or prevented by the presence of ammonium hydroxide, tartrates or citrates. The presence of 0.5 M sodium chloride aids the formation of a crystalline precipitate. Between 0.4 and 133 mg of perrhenate may be determined in 25–60 ml of solution. The drying conditions for tetraphenylarsonium perrhenate have been established thermogravimetrically by Tribalat and Duval<sup>8</sup> to be between 126 and 185°.

Tribalat<sup>9</sup> has examined the solvent extraction of rhenium from molybdenite ores. After preliminary treatment of the ores, rhenium in the form of tetraphenylarsonium perrhenate is extracted quantitatively from solutions of pH between 8 and 9 with chloroform. In this pH region, molybdenum remains in the aqueous phase. The colorimetric finish is made by reaction of the perrhenate with thiocyanate and tin(II) chloride to give the yellow thiocyanatorhenate(VI) species. The method can be applied to ores containing >100 ppM ( $M = 10^9$ ) rhenium. Further studies by Tribalat and co-workers suggest that the absorbance of the thiocyanate-complex is best measured in isoamyl alcohol.<sup>10</sup> Beeston and Lewis<sup>11</sup> report that after chloroform extraction of the perrhenate, the complex can be transferred into 6M hydrochloric acid directly without evaporation of the chloroform and under these conditions the coloured thiocyanato-complex is very stable. The application of the tetraphenylarsonium extraction procedure to tungsten-rhenium and molybdenum-rhenium alloys containing 1% rhenium has been described by Andrew and Gentry.<sup>12</sup>

Richardson<sup>13</sup> has described the determination of manganese at the 5-ppm level in luminescent-quality calcium carbonate. After dissolution of the sample, potassium metaperiodate is used to oxidize manganese(II) to permanganate, which is afterwards extracted into chloroform as tetraphenylarsonium permanganate and measured directly at 532 nm against chloroform. The results are reliable to 0.1 ppm.

Glover and Rosen<sup>14</sup> have assayed ammonium perchlorate by precipitation with tetraphenylarsonium chloride. Recoveries of 99.8% were reported. Neither bromate nor chlorate interferes in the determination at levels up to 0.5%. A conductometric titration technique was applied to the same problem by Baczuk and Bolleter.<sup>15</sup> Results with a precision of  $\pm 0.16\%$  were obtained; potassium chloride, chlorate, bromide, bromate, nitrate and chromate at 1:1 weight ratios did not affect the determination. Baczuk and Dubois<sup>16</sup> have since examined the use of a perchlorate ion-specific electrode to follow the precipitation of perchlorate, again for the assay of ammonium perchlorate. Large amounts of some simple anions distort the titration curves and should be corrected for by adding equivalent amounts of these anions in the standardization of the titrant. The interference of chloride, bromide, bromate, fluoride, sulphate, nitrate and chromate is overcome by this technique. Errors are caused by a subquantitative precipitation of chlorate when present above 0.02M. Permanganate, periodate and dichromate are precipitated quantitatively. On

replicate analysis of three samples, overall 95% confidence limits were  $\pm 0.16\%$ . The solvent extraction of technetium as the tetraphenylarsonium pertechnetate has been studied in detail by Tribalat and Beydon<sup>17,18</sup> and the method applied to the separation of this element (produced artificially) from molybdenum or uranium.

Beck and Beilstein<sup>19</sup> have examined the effects of pH on the extraction of a large number of oxy-anions with tetraphenylarsonium chloride and have recorded the partition coefficients.

(b) Mercury(II),<sup>20</sup> tin(IV),<sup>20</sup> cadmium<sup>20</sup> and zinc<sup>20</sup> may be precipitated quantitatively in the presence of an excess of sodium chloride as their chloro-anions, with tetraphenylarsonium chloride. It is necessary to add an excess of reagent and to back-titrate with iodine since no suitable wash-liquor for the precipitate was found. Between 0.5 and 100 mg of mercury(II) in 1.0–2.5M sodium chloride may be determined in 30–120 ml of sample solution to within 0.06 mg. Free acids (except nitric acid) in concentrations of 0.2–1.0M do not interfere. The precipitate does not form in alkaline conditions. Permanganate, perrhenate, perchlorate, periodate, iodide, bromide, fluoride, tungstate, molybdate, chromate, thiocyanate, bismuth, platinum(IV), tin(IV), zinc, cadmium, thallium(III) and those ions which react with iodide ion or iodine interfere. The interference of copper(II), tin(IV), manganese(II), iron(III) and titanium(IV) may be overcome by selective masking. Tin (0.80–84.0 mg) in a volume of 30–120 ml may be determined within  $\pm 0.04$  mg by precipitation of the tetraphenylarsonium salt followed by titration of the excess of tetraphenylarsonium chloride or by direct titration of the separated precipitate. The precipitation should be carried out in 0.4–2.0M hydrochloric acid and 1.5–3.0M sodium chloride, dependent on the amount of tin present. Iron(III) and more than 25 mg of iron(II), platinum(IV), gold(III), bismuth, mercury(II), cadmium, zinc, thallium(III), antimony(III), arsenic(III), uranium(VI), fluoride, oxalate, phosphate, acetate, citrate and all ions precipitated by the reagent must be absent.

Cadmium and zinc may be precipitated from 3.0–3.5M sodium chloride solutions. The interferences are similar to those for the tin determination except that interference by manganese, cobalt, copper and iron is more serious; small amounts of tin may be masked by the addition of tartrate.

Menis *et al.*<sup>21</sup> have examined the precipitation of mercury(II) in the presence of chloride and nitrate ion with tetraphenylarsonium chloride. The precipitate was shown to be  $[(C_6H_5)_4As^+][HgCl_2NO_3^-]$ . The reaction is quantitative and can be followed amperometrically in the region from 0 to  $-0.5$  V *vs.* S.C.E. Between 0.025 and 2.30 mg of mercury(II) can be titrated with a coefficient of variation of 3%. A detailed examination of interferences was reported.

Smith<sup>22</sup> reports the gravimetric determination of thallium(III) by precipitation of tetrachlorothallate(III). Hydrogen peroxide is used to oxidize thallium(I). Excess of hydrochloric acid must be present during the precipitation. The precipitate is washed with hydrochloric acid to prevent hydrolysis. Results accurate to within 0.2 mg at the 100-mg level were obtained.

The chloroaurate(III) ion forms a chloroform-soluble precipitate from aqueous solution with the tetraphenylarsonium cation. Murphy and Affsprung<sup>23</sup> report that 7–40 ppm of gold can be determined spectrophotometrically by measuring the absorbance of chloroform extracts at 323 nm. Interference studies were made; iron

caused the most serious interference but this can be suppressed by fluoride. None of the platinum group metals interferes with the determination except when present in concentrations greater than one-tenth that of the gold.

Potratz and Rosen<sup>24</sup> in a study of various onium ions found that the precipitation of bismuth in the presence of excess of iodide could be used as a spot test for bismuth. The sensitivity of the test,  $2 \mu\text{g/ml}$ , was the same as that using cinchonine. The reaction has been studied further<sup>25</sup> and transmittance measurements of chloroform extracts of tetraphenylarsonium tetraiodobismuthate at 510 nm can be used for estimations of between 1 and  $5 \mu\text{g}$  of bismuth with a precision of  $\pm 5\%$ . Interference studies are reported.

Bode<sup>26</sup> reports that after reduction of selenium with sulphur dioxide, tellurium can be determined gravimetrically or titrimetrically with tetraphenylarsonium chloride since the precipitation of tetraphenylarsonium hexachlorotellurate is quantitative in the presence of  $4\text{-}5M$  hydrochloric acid. Results to within  $\pm 0\cdot5\%$  at the  $3\cdot0\text{-mg}$  level, even in the presence of a tenfold excess of selenium, are reported. Interferences were examined and comprise those oxy-anions or chloro-anions which are precipitated by the reagent.

A detailed study of the conditions for the extraction into chloroform of the fluoroborate ion with the tetraphenylarsonium cation is reported by Coursier *et al.*<sup>27</sup> After development of colour with curcumin  $0\cdot1\text{-}1 \mu\text{g}$  of boron can be determined readily. Ducret and Seguin,<sup>28</sup> using the same procedure, showed that it is possible to determine traces of boron in silicon. A direct gravimetric procedure has been developed by Affsprung and Archer.<sup>29</sup> Standard deviations of  $0\cdot1\%$  at the  $30\text{-mg}$  level for the determination of ammonium fluoroborate are reported. An indirect method, based on the absorbance of excess of reagent at 220 nm gave results correct to within  $1\%$  for similar sample sizes.

Affsprung and Archer<sup>30</sup> have examined the amperometric titration of hexafluorophosphate, using the tetraphenylarsonium ion as the indicator ion. The results compared favourably with the nitron procedure. The reaction can also be used in a simple direct gravimetric procedure.<sup>31</sup> No interference was found from ions commonly occurring with the hexafluorophosphate ion. The hexafluoroantimonate ion is rapidly hydrolysed in aqueous solutions. Archer and Twelves<sup>32</sup> avoided the problems of hydrolysis by dissolving samples in dimethylformamide and adding the precipitant, tetraphenylarsonium chloride, as a concentrated aqueous solution. Quantitative results were obtained at the  $0\cdot1\text{-g}$  level, the standard deviation being  $0\cdot4\%$ . Fluoride does not interfere, but any anion which forms a precipitate with the reagent must be absent.

Reactions of the platinum group metals with tetraphenylarsonium and -phosphonium salts has been studied by several workers. Neeb<sup>33</sup> reports spot-tests based on the microcrystalline form of precipitates of osmium(IV), in the presence of excess of chloride, with tetraphenylarsonium chloride, tetraphenylphosphonium chloride and also with triphenylmethylarsonium iodide. The sensitivities are of the order of  $0\cdot2 \mu\text{g/ml}$ . The presence of excess of ruthenium reduces the sensitivities. Similar studies<sup>34</sup> have been made for iridium, palladium and platinum. Osmium<sup>35</sup> can be extracted as hexachloro-osmate(IV) with tetraphenylarsonium chloride into chloroform and can be determined at 346 or 375 nm; up to a 200-fold excess of ruthenium can be tolerated. The conditions for a gravimetric determination<sup>36</sup> have been reported, following an investigation of the solubilities of a large range of arsonium and phosphonium



chloro-osmates. Neeb<sup>37</sup> examined the precipitation of chlorocomplexes of iridium and describes the determination of iridium in the range .15–15 mg to within 1%. Bode<sup>38</sup> reports the determination of platinum based on the precipitation of tetraphenylarsonium hexabromoplatinate(IV) to within 0.6% at the 1–10 mg level.

(c) The extraction of tetrathiocyanatocobaltate(II) by tetraphenylarsonium chloride into chloroform was first put forward as a spot-test for cobalt by Potratz and Rosen<sup>24</sup> at levels of 0.1  $\mu\text{g/ml}$ . The addition of fluoride and thiosulphate masks the interference of iron(III), copper(II), uranium(VI), palladium(II), platinum(IV) and bismuth(III). The procedure has been developed by Affsprung *et al.*<sup>39</sup> for the spectrophotometric determination of traces of cobalt in uranium materials, alloy steels and nickel–copper alloys. No previous separation of iron, nickel or copper is required since fluoride and thiosulphate are effective in masking iron and copper respectively and nickel is not extracted. Results are within 1% of NBS. specification values for the standard steels examined, which covered the range 0.08–8% cobalt. Their findings were confirmed by Pepkowitz and Marley,<sup>40</sup> who analysed a series of NBS stainless steels. Khattak and Magee<sup>41</sup> have examined the precipitation of the tetrathiocyanatocobaltate(II). Although precipitation is complete the method cannot be used gravimetrically because of co-precipitation of tetraphenylarsonium thiocyanate. Quantitative results, even in the presence of 100-fold excess of nickel, to within 4% at the 2 mg level were obtained by diffuse reflectance spectrophotometry. The Kubelka-Munk relationship was obeyed. Magee and Kattak<sup>42</sup> have shown that the extraction of tetraphenylarsonium tetrathiocyanatopalladate(II) into chloroform and measurement of absorbance at 320 nm allows palladium estimation at the 0.5–4  $\mu\text{g/ml}$  level to within 2%. Platinum, rhodium and ruthenium can be tolerated at ratios up to 5:1; osmium interferes seriously. Iron should be masked with phosphate to avoid the formation of extractable fluorides of metals in the platinum group.

Affsprung and Robinson<sup>43</sup> have developed a rapid and accurate spectrophotometric method for niobium based on the extraction of tetraphenylarsonium thiocyanatoniobate(V) into 9:2 chloroform/acetone solution and measurement of absorbance at 390 nm. Niobium is masked before a separation step in which the interfering metals, molybdenum, tungsten and iron, are removed by reduction and extraction. Niobium is subsequently demasked with boric acid. The method was applied to NBS steels and alloy samples covering a range of 0.013–3.15% niobium. Results to within 2% of the specifications were obtained at levels above 0.2%.

Affsprung and Murphy<sup>44</sup> have developed a method for the spectrophotometric determination of tungsten. After reduction with tin(II) chloride in 6–9M hydrochloric acid, tetraphenylarsonium chloride and potassium thiocyanate are added and the complex,  $[(\text{C}_6\text{H}_5)_4\text{As}^+][\text{W}(\text{OH})_2(\text{SCN})_4^-]$ , is extracted into chloroform. The absorbance of the extract is measured at 406 nm. The method is selective, under the conditions described, for tungsten after niobium has been masked with fluoride. The method was applied to a series of NBS steels and alloy samples with tungsten contents in the range 0.5–18%. Excellent agreement with specification values was obtained.

(d) A microgravimetric determination of germanium as tetraphenylarsonium molybdo-germanate has been described by Labbé.<sup>45</sup> Standard deviations of 0.2% were found at the 1.5-mg germanium level. Interference studies are reported. The composition

of the precipitate,  $[(C_6H_5)_4As^+]_4[GeMo_{12}O_{40}^{4-}]$ , was confirmed by thermal analysis. This system was studied further<sup>46</sup> along with that of the molybdosilicate by gravimetric and thermogravimetric techniques as well as by infrared absorption.

Ziegler and Glemser<sup>47</sup> describe the detection of microgram amounts of titanium by extraction of the yellow sulphosalicylate complex anion at pH 4.6 into chloroform with tetraphenylarsonium chloride. The reaction was found to be specific if any iron(III) present is reduced to iron(II) with ascorbic acid.

Tagliavini and Zanella<sup>48</sup> have examined the potentiometric titration of  $R_{(4-n)}SnCl_n$  compounds (where R = Me, Et, Pr, Bu, Ph;  $n = 2, 3$ ) in acetonitrile media. Evidence for penta-co-ordinated  $R_{(4-n)}SnCl_{(1+)}^-$  complexes was obtained. The stability of these complexes was examined as a function of R.

An improved absorption technique using potassium bromide discs prepared from precipitates formed with various anions and tetraphenylarsonium chloride has been developed by Al-Kayssi and Magee<sup>49</sup> for the identification of these anions. The presence of pertechnetate, perrhenate, thiocyanate, persulphate, perchlorate, chlorate, permanganate, periodate, ferricyanide, ferrocyanide, thiosulphate, chromate or dichromate, molybdate and tungstate can be rapidly and reliably confirmed much more conveniently than by classical methods.

Kolthoff and Johnson<sup>50</sup> found that traces of tetraphenylarsonium chloride catalyse the reduction of tin(IV) to tin(II) at a dropping mercury electrode. The diffusion current of the improved wave is more easily measured and is more suitable for quantitative work. Because the catalysed wave is fully developed at more positive potentials diffusion currents unaffected by lead at concentrations less than 0.01M may be measured.

#### *Reactions of the triphenylmethylarsonium cation*

*Triphenylmethylarsonium chloride.* This has been studied by Gibson and his co-workers who have reported a series of titrations with extractive end-points, in addition to colorimetric applications. The titrations are interesting in that they obviate the need for redox indicators to detect the end-point of certain reactions and allow the titration of highly coloured and turbid solutions. The triphenylmethylarsonium cation forms highly coloured chloroform-soluble compounds with permanganate,<sup>51</sup> dichromate<sup>52</sup> and iodine.<sup>53</sup> End-points in titrations are located by extraction of excess of oxidants; blanks are of the order of 0.03–0.06 ml at 0.1N concentrations. The procedure has been extended to the EDTA titration of cobalt<sup>54</sup> by using the extraction of triphenylmethylarsonium tetrathiocyanatocobaltate(II) to indicate the end-point. Copper, nickel, iron, chromium and vanadium<sup>55</sup> have been determined by back-titration of excess of EDTA with standard cobalt solutions. Results accurate to within 1.0% were reported.

Colorimetric determinations for iron, copper and cobalt based on extraction of thiocyanato-complexes have been proposed. The procedure for iron<sup>56</sup> covers the range 1–10  $\mu\text{g/ml}$ . A 1000-fold excess of chromium and nickel and a 20-fold excess of cobalt do not interfere. The dissociation equilibria of the complex  $[Ph_3MeAs^+]_3[Fe(SCN)_6]^{3-}$  have been studied.<sup>57</sup> The procedure for copper<sup>58</sup> covers the range 10–100  $\mu\text{g/ml}$  and the precision is 2%. The tolerance for nickel, manganese, aluminium and cadmium is such that copper can be estimated in most of its common alloys without previous separation. The interference by chromium and iron is such that only

a simple partial separation is required. Cobalt should be absent. Cobalt<sup>59</sup> can be estimated in the range 10–100  $\mu\text{g/ml}$ ; iron(III) is masked by fluoride and copper by thiosulphate. Results accurate to 2% are reported. The colorimetric estimation of nickel<sup>60</sup> involves the formation of the triphenylmethylarsonium dithio-oxalatonickelate(II) complex which is extracted into an acetophenone/chloroform mixture. The range is 25–250  $\mu\text{g/ml}$  of nickel; errors were not greater than 1%. Iron, cobalt and copper interfere seriously and their removal is described.

Antimony<sup>61</sup> may be extracted into *o*-dichlorobenzene as the tetraiodo complex, over the range 10–100  $\mu\text{g/ml}$ ; accuracies of 2% were found. Simple partial separations are suggested so that this accuracy is maintained in the presence of the commonly interfering metals including lead, bismuth, copper, tin and arsenic.

The microdetection<sup>62</sup> and estimation<sup>63</sup> of cadmium both gravimetrically and nephelometrically, based on the sparingly soluble tetraiodocadmiate complex and covering the ranges 1–100  $\mu\text{g/ml}$  and 1–100 mg respectively have been described. A 100-fold excess of zinc may be tolerated; silver, lead, mercury, copper, bismuth, antimony and arsenic interfere and may be removed by boiling the acid solution with iron wire and filtering before addition of the triphenylmethylarsonium chloride. Bismuth<sup>64</sup> may be detected at 0.8  $\mu\text{g/ml}$  by precipitation of  $[\text{Ph}_3\text{MeAs}^+][\text{BiI}_4^-]$ .

#### *Reactions of the tetraphenylphosphonium cation*

Tetraphenylphosphonium bromide was first examined as a reagent for bismuth by Potratz and Rosen,<sup>24</sup> who showed that 2  $\mu\text{g}$  of bismuth per ml could be detected readily. The reaction has been examined by Matano and Kawase<sup>65</sup> who show that chloroform extraction of tetraphenylphosphonium tetraiodobismuthate and measurement at 505 nm permits the rapid determination of 10–120  $\mu\text{g}$  of bismuth. Interference studies are reported; that of antimony may be masked by the addition of excess of tartrate ion.

Willard and Perkins<sup>66</sup> showed that tetraphenylphosphonium chloride in the presence of sodium chloride quantitatively precipitates complex chloro-anions of tin(IV), mercury(II) and cadmium. It is necessary to add excess of reagent and to back-titrate potentiometrically with iodine since no suitable wash-liquor for the precipitates was found.

Tetraphenylphosphonium permanganate, perrhenate and perchlorate are insoluble in cold water and both gravimetric and titrimetric methods are possible. For periodate, however, only the titrimetric method is suitable for quantitative work. Average errors are  $\pm 0.06$  mg for 50 mg of ion sought. Nezu<sup>67</sup> has examined in detail the amperometric titration of permanganate and perchlorate with tetraphenylphosphonium chloride, following an earlier preliminary study.<sup>68</sup> Permanganate ( $10^{-3}M$ ) in 0.5M sodium sulphate could be titrated with an error of  $\pm 2.0\%$ . Similar results for perchlorate in 2.0M sodium sulphate were reported. When manganese has to be determined in highly coloured solution or in the presence of thiocyanate, persulphate, polymolybdate, or polytungstate, Medoks and Maslova<sup>69</sup> recommend oxidation of manganese and precipitation of permanganate with excess of tetraphenylphosphonium bromide. The precipitate is treated with excess of standard oxalic acid solution which is back-titrated with permanganate. The procedure is very precise.

Neeb<sup>70</sup> reports the spectrophotometric determination of iridium by solvent extraction into chloroform with tetraphenylphosphonium chloride. Other platinum group

metals interfere and must be removed previously. In a later study Neeb<sup>71</sup> examined the determination of molybdenum after reduction with tin(II) and extraction of the thiocyanato-molybdate(V) complex into chloroform. Relative standard deviations of 1% for 3–5 mg of molybdenum were obtained. A range of possible interferences was examined. A 50-fold excess of tungsten produces a 7% positive error.

Bock and Jainz<sup>72</sup> studied the effects of pH on the solvent extraction of various anions and showed that iodide, thiocyanate, perchlorate, permanganate, perrhenate, chlorate and dichromate can be extracted readily from aqueous solution into chloroform by tetraphenylphosphonium chloride and thus can be separated from various other anions. A theory of ion-association extraction using tetraphenylarsonium, triphenylsulphonium and tetraphenylphosphonium ions has been put forward by Ružička and Zeman<sup>73</sup> and these reagents have been shown to be suitable for selective substoichiometric separations. The substoichiometric determination of manganese, rhenium and iodine by activation analysis should be possible, but the use of the reagents for isotope dilution seems doubtful. The amperometric titration of tetraphenylphosphonium, triphenylsulphonium and triphenylselenonium chlorides with an error of  $\pm 3.0\%$  at concentrations of  $10^{-3}M$ , with sodium tetraphenylborate, has been reported by Nezu.<sup>74</sup> Tribalat<sup>75</sup> suggests that tetraphenylphosphonium or tetraphenylarsonium chloride can be used to separate and determine traces of rhenium in natural products by extraction of perrhenate into chloroform. Later triphenylbenzylphosphonium chloride was put forward by Tribalat<sup>76</sup> as an alternative extractant. 3,4-Dichlorobenzyltriphenylphosphonium chloride was suggested by Neeb and Khan-Boluki<sup>77</sup> as an alternative to tetraphenylarsonium chloride used in Neeb's previous procedure<sup>70</sup> for the determination of osmium and iridium by extraction of the hexachloro-osmate(IV) anion.

#### *Reactions of the tetraphenylstibonium cation*

Potratz and Rosen<sup>24</sup> were the first to suggest the use of the tetraphenylstibonium ion as a spot-test reagent for bismuth, for which it has a sensitivity of  $2 \mu\text{g/ml}$ . Perchlorate<sup>66</sup> has been determined gravimetrically in the presence of chlorate; chlorate is reduced with bisulphite before the addition of the reagent. Morris<sup>78</sup> reports the amperometric titration of perchlorate at  $-0.88 \text{ V vs. S.C.E.}$  at concentrations of  $2-4 \times 10^{-2}M$  to within 1.5%. Chloride, chlorate, phosphate, sulphate and nitrate do not interfere.

By amperometric titration at a dropping mercury electrode at  $-0.72 \text{ V}$ , Shinagawa, Matsuo and Okashita<sup>79</sup> were able to determine bismuth and mercury to within 2% and 3% respectively.

Studies on the solubilities of tetraphenylstibonium salts<sup>80</sup> of inorganic ions suggest that fluoride can be determined by solvent extraction. Bowen and Rood<sup>81</sup> have developed a rapid separation procedure for producing carrier-free fluorine-18 from lithium. After neutron irradiation the lithium carbonate sample is dissolved in dilute sulphuric acid solution and the fluorine-18 is extracted into chloroform as tetraphenylstibonium fluoride which is back-extracted into dilute base. This procedure gives more than an 80% recovery of fluorine-18 from a 20-g lithium carbonate target in 30 min. The variation of distribution ratio with pH and with tetraphenylstibonium, fluoride and salt concentration was studied. Ovenberg and Morris<sup>82</sup> report that aqueous solutions of fluoride ion may

be titrated with tetraphenylstibonium sulphate. The relative error is  $\pm 1.0\%$  over the range  $1-50 \times 10^{-3} M$  fluoride. Fluoride is extracted into chloroform as the ion-pair  $[(C_6H_5)_4Sb]^+F^-$ . The aqueous phase fluoride activity is monitored potentiometrically with a fluoride-sensitive electrode. Equal initial volumes of aqueous phase (pH 4-5) and extractant are used. The aqueous phase is made  $0.1 M$  in sodium sulphate to inhibit emulsification and to facilitate phase separation. Thirty sec of intimate phase contact (stirring) and 15 sec for phase separation are required between additions of titrant. Phosphate, arsenate, arsenite and sulphate do not interfere. Nitrate and perchlorate interfere but are readily removed by the addition of tetraphenylarsonium sulphate; nitrate forms an extractable ion-pair with the reagent while perchlorate forms a very insoluble salt. Sulphite and nitrite interferences are removed by oxidation with hydrogen peroxide to sulphate, which does not interfere, and to nitrate which is removed as described above. The halides and thiocyanate interfere and are removed by silver nitrate precipitation. Conditional partition coefficients for the fluoride extraction were measured and were used to demonstrate agreement between theoretical titration curves and experiment.

Affsprung and May<sup>83</sup> have used tetraphenylstibonium sulphate for the qualitative identification of organic acids. The derivatives are small needle-shaped crystals obtained in good yields. The melting points are sufficiently sharp and far enough apart for easy differentiation of many organic acids.

#### *Reactions with triphenyltin chloride*

Krause and Becker<sup>84</sup> in a study of aryltin compounds noted that "triphenyltin fluoride is sparingly soluble in cold alcohol, ether and water", and that "fluoride can be quantitatively precipitated with triphenyltin chloride". Later, Allen and Furman<sup>85</sup> examined the method in detail and determined 0.2-50 mg of fluoride gravimetrically in 70% ethanol solutions. Halides (other than fluoride), nitrate and sulphate do not interfere, but carbonate, phosphate and silicate must be removed. A procedure involving interaction at a chloroform-water interface has been put forward by Ballezo and Schiffner.<sup>86,87</sup> The reagent is in the chloroform and the fluoride is in the aqueous layer (pH 4-8). The precipitation is complete after 1-1½ hr stirring. Between 10 and 150 µg of fluoride can be determined in the presence of phosphate, borate, aluminium, zirconium or iron. Other organotin cations were examined<sup>86</sup> but these were no more convenient than the triphenyltin ion.

Triphenyltin compounds are used as fungicides, and residues are usually determined with dithizone<sup>88,89</sup> although the compounds are electroactive.<sup>90,91</sup>

Bock *et al.*<sup>92</sup> have studied the effects of pH on the solvent extraction into benzene of numerous inorganic and organic anions with triphenyltin hydroxide and suggest that several separations could be developed.

#### *Reactions of the triphenylsulphonium, -selenonium and -telluronium cations*

*Triphenylsulphonium chloride.* This was first suggested as a reagent for the detection of bismuth and cobalt by Potratz and Rosen.<sup>24</sup>

Shinagawa *et al.*<sup>93</sup> showed that bismuth and mercury may be titrated amperometrically as their chloro-complexes, within 1% error, with triphenylsulphonium chloride. The effects of pH on the solvent extraction of triphenylsulphonium salts were studied by Bock and Hummel.<sup>94</sup> Perchlorate, permanganate, perrhenate, iodide and

dichromate may be readily extracted from aqueous solution. The reagent shows a tendency to decompose.

*Triphenylselenonium cation.* This was examined first as a reagent for bismuth and cobalt by Potratz and Rosen.<sup>24</sup> Ziegler and Pohl<sup>95</sup> show that the ion is suitable for the detection of 5  $\mu\text{g}$  of perchlorate in the presence of a 100-fold excess of chlorate. Further, the conditions are described for the estimation of chromium in cast iron and steels containing manganese, vanadium and molybdenum. Good agreement with specifications was obtained for determination in standard steels. The precipitation of triphenylselenonium ion with tetraphenylborate anion was shown to be quantitative. Ziegler and Riedel<sup>96</sup> show that 10–200  $\mu\text{g}$  of mercury(II) can be extracted as the chloro-complex into methylene chloride, and afterwards can be estimated at 310 nm as colloidal mercury(II) sulphide in the methylene chloride phase. Shinagawa *et al.*<sup>97,98</sup> show that the amperometric titration of bismuth as either tetraiodobismuthate or tetrachlorobismuthate with triphenylselenonium chloride in 0.2–0.3M hydrochloric acid allows determinations to within  $\pm 1.0\%$  to be made.

*Triphenyltelluronium cation.* This was first examined as a reagent by Potratz and Rosen<sup>24</sup> who described spot tests for cobalt and bismuth based on precipitation of the thiocyanate and iodo-complexes respectively. Shinagawa *et al.*<sup>99</sup> have studied the bismuth reaction and have shown that it is sensitive to a few tenths  $\mu\text{g}$  and may be followed polarographically.

#### COMPARISON OF METHODS

In general the reactions of the onium ions are very similar. Any advantage which one onium ion has in a particular determination arises from a slightly more favourable solubility product or extractability of the ion-association complex formed with the ion to be determined. The availability or ease of preparation of salts of the onium ion must also be taken into account in selecting a suitable onium reagent.

Analytical methods in which onium compounds are used compare very favourably with other methods, and in many cases have distinct advantages. Thiocyanato extraction methods for iron,<sup>56</sup> cobalt<sup>39</sup> and tungsten,<sup>44</sup> for example, are improved if the tetraphenylarsonium salt rather than the free acid is extracted. The pH of the aqueous phase is less critical and the colour of each extract is much more stable. Similarly, the extraction of bis(dithio-oxalato)nickelate(II) as its triphenylmethylarsonium salt stabilizes the complex anion, and provides one of the most sensitive and satisfactory colorimetric methods for nickel.<sup>60</sup>

The solvent extraction procedures developed for rhenium,<sup>7–11</sup> technetium<sup>17,18</sup> and boron<sup>27–29</sup> with tetraphenylarsonium chloride have improved greatly the selectivity, sensitivity and scope of methods of determining these elements. The method for gold<sup>23</sup> is extremely simple and rapid; that for manganese<sup>13</sup> is reported to be highly selective and more accurate, reliable and sensitive than any other permanganate colorimetric method.

Tetraphenylphosphonium salts are reported to be generally more soluble than the corresponding tetraphenylarsonium salts.<sup>66</sup> The reactions of these two ions are very similar, and there appears to be no analytical advantage in using the tetraphenylphosphonium ion. The latter is more easily synthesized<sup>66</sup> but the cost of their commercially available chlorides is similar. The solubility of tetraphenylstibonium chloride is so low<sup>66</sup> that it is not a useful reagent except possibly for the extraction of fluoride.<sup>80,81</sup>

Similarly the triphenyltin ion is probably only really useful for the precipitation of fluoride.<sup>84-87</sup>

Triphenylmethylarsonium salts, such as the permanganate and dichromate, have a slightly higher water solubility than the corresponding tetraphenylarsonium salts, and triphenylmethylarsonium chloride has found considerable use as an extractive indicator.<sup>51-55</sup> It appears that tetraphenylarsonium permanganate and dichromate are so readily extracted into chloroform that there is a potential danger of obtaining false endpoints.<sup>51</sup> Triphenylmethylarsonium iodide and molybdate are water-soluble and for this reason the triphenylmethylarsonium ion is more selective than other onium ions.<sup>59</sup> Again it is prepared more easily than the tetraphenylarsonium and tetraphenylphosphonium ions,<sup>59</sup> but commercially its chloride is priced similarly and is not so readily available.

**Zusammenfassung**—Es wird ein Überblick gegeben über Reaktionen und analytische Anwendungen folgender Verbindungen: der Kationen Tetraphenylphosphonium, -arsonium und -stibonium, Triphenylmethylarsonium, Triphenylsulfonium, -selenonium und -telluronium sowie Triphenylzinn mit Oxyanionen sowie der anionschen Halogeno- und Thiocyanatokomplexe.

**Résumé**—On étudie les réactions et les applications analytiques des cations tétraphényl-phosphonium, -arsonium et -stibonium, triphénylméthylarsonium, triphényl-sulfonium, -sélénonium et -tellurnoium et triphénylétain avec des oxy-anions et des complexes halo- et thiocyanato-anioniques.

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## COULOMETRISCHE METALLOMETRIE ELEKTROLYTISCH ERZEUGTER KUPRIION ALS COULOMETRISCHER TITRANT

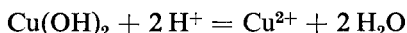
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**Zusammenfassung**—Es wurden die Bedingungen für eine quantitative elektrolytische Auflösung des Kupfers und zur anodischen Erzeugung der Kupriionen aufgefunden und eine neue coulometrische kuprimetrische Bestimmung von Anthranilsäure, mit einer amperometrischen Endpunktbestimmung mit einem Indikatorsystem aus zwei polarisierten Kupferelektroden, ausgearbeitet.

IM BESTREBEN die coulometrische Metallometrie<sup>1</sup> auf eine grössere Anzahl von Metallen zur coulometrischen quantitativen Bestimmung durch anodisch erzeugte Metallionen auszudehnen und weiter anzuwenden, wurde die anodische Polarisierung einer Elektrode von einem metallischen Kupfer in dieser Beziehung untersucht und dabei festgestellt, dass unter bestimmten Bedingungen Kupriionen quantitativ, oder mit konstanter Ausbeute, durch anodische Oxydation des Kupfer erzeugt werden können.<sup>2</sup>

Bei der anodischen Oxydation des Kupfers bis zu Kupriionen ist das pH der Lösung durch die Reaktion



begrenzt und die Aktivität der Kupriionen ist durch die Gleichung

$$\log a_{\text{Cu}^{2+}} = \frac{\mu^0\text{Cu(OH)}_2 - \mu^0\text{Cu}^{2+} - 2\mu^0\text{H}_2\text{O}}{1363} - 2\text{pH}$$

$$\log a_{\text{Cu}^{2+}} = 9,21 - 2\text{pH}$$

geregelt.

Zur Prüfung der metallometrischen analytischen Anwendungsmöglichkeit der elektrolytisch erzeugten Kupriionen, wurde die Fällung und quantitative Bestimmung von Anthranilsäure, untersucht, die ein wohl definiertes und schwer lösliches 1:2 Kupferanthranilat bildet.

Durch Aufnahme der Strom-Potentialkurven unter verschiedenen Bedingungen in wässrigen Lösungen der Anthranilsäure und des Natriumanthranilats, konnte durch Extrapolation das Potential  $e_h$  einer Arbeitselektrode aus Kupfer, bei einer Stromdichte von 0 mA/cm<sup>2</sup> bestimmt werden. Dieses Potential  $e_h$  in einem Anolyten, der aus einer 0,1M Natriumsulfatlösung besteht und in 100 ml, bei pH = 7,0, 102,2 mg Anthranilsäure in Form von Natriumanthranilat enthält, beträgt 0,29 V. Der Wert des gemessenen Potentials der Kupferanode in der neutralen Anthranilat-lösung bei Anwesenheit der Kupriionen, deren Konzentration durch Ionenprodukt des Kupferanthranilats, im Gleichgewicht mit den Kupriionen in der Reaktionsschicht der Kupferanode, bedingt ist, weicht proportional der Ionenkonzentration von dem bekannten Wert des Potentials für Kupfer<sup>3</sup> ab.

Um immer mit einer definierten und gleichen Oberfläche und Struktur der Kupferanode zu arbeiten, diente bei allen Untersuchungen als Kupferanode ein verkupferetes Kupfer oder Platinblech, das im Elektrolyten und unter Bedingungen des Kupfercoulometers für jede Potentialmessung oder metallometrische coulometrische Anwendung, nach Wascher in Salpetersäure, frisch bereitet wurde, mit einer Kupfermenge die mindestens um 50% grösser, als die für die metallometrische Auflösung benötigte war.

Die elektrolytisch gelöste Kupriionen bilden in der neutralen Lösung mit den vorhandenen Anthranilationen einen hell grünen Niederschlag mit der Zusammensetzung  $\text{Cu}(\text{C}_7\text{H}_5\text{O}_2\text{N})_2$ . Das durch anodische Auflösung des Kupfers in einem Anolyten, bei  $\text{pH} = 7,0$ , der auf 200 ml einer 0,05M Natriumsulfatlösung 340 mg Anthranilsäure als Natriumanthranilat enthielt,  $i = 49,9$  mA, bei einer Anodenoberfläche von  $12 \text{ cm}^2$ , gebildete Kupferanthranilat zeigte durch Analyse die folgende Zusammensetzung:  $\text{Cu}(\text{C}_7\text{H}_5\text{ON})_2$ ; berechnet: C, 50,06; H, 3,60; N, 8,34; Cu, 18,93%; gefunden: C, 49,7; H, 3,9; N, 8,1; Cu, 19,4%.

Das bei einem bedeutenden Überschuss von Kupriionen gebildete Kupferanthranilat, welches analytisch unbrauchbare Resultate mit einem positiven Fehler verursacht (siehe Tabelle) hat der ausgeführten Analysen nach, dieselbe normale Zusammensetzung des Kupferanthranilats, sodass die festgestellten analytischen Fehler wohl der Adsorption des Kupriions durch das gefällte Anthranilat und einer Bildung von Kuprihydroxyd zuzuschreiben wäre.

#### *Amperometrische Endpunktbestimmung*

Um eine Einsicht in den Verlauf der anodischen Kupriionen- und der Kuprianthranilatbildung zu erlangen und zur Endpunktbestimmung wurde die amperometrische Methode angewandt. Zu diesem Zweck wurde die Anwendungsmöglichkeit verschiedener amperometrischer Indikatorsysteme bei der Kuprimetrischen Bestimmung der Anthranilsäure untersucht. Es zeigte sich dabei, dass die Empfindlichkeit eines Indikatorsystems mit einer polarisierten Platin- oder Kupferelektrode von einer Oberfläche von  $0,5 \text{ cm}^2$ , bei einem Potentialunterschied von 50 mV und einer Generatorstromstärke von 20 mA, in einer 0,07M Natriumsulfatlösung etwa  $0,2\text{--}0,3 \mu\text{A}/\text{sec}$  beträgt, wobei eine Vergrößerung der Oberfläche keinen bedeutenden Einfluss auf die Empfindlichkeit des Systems ausübte. Die Empfindlichkeit eines Systems mit einer Quecksilbertropfenelektrode beim Polarisationspotential von  $-0,85 \text{ V}$  gegen eine gesättigte Kalomelektrode, bei einer Generatorstromstärke von 20 mA in einer 0,05 bis 0,25M Natriumsulfatlösung, unter Zugabe von 0,1% Gelatine und Entfernen des Sauerstoffs durch Einleiten von Wasserstoffgas, beträgt  $0,002 \mu\text{A}/\text{sec}$ . Bei allen untersuchten Systemen wurden die Indikatorstromstärken 15 bis 30 Sekunden nach Einschalten des Indikatorstromkreises registriert.

Die Untersuchung der Indikatorsysteme mit zwei polarisierten Kupfer- oder Platinelektroden wurde durch Bestimmung der Änderung der Indikatorstromstärke mit der Änderung der Potentialdifferenz zwischen den Indikatorelektroden zur Abgrenzung des Gebietes geringerer Indikatorstromänderung mit der Potentialdifferenz ausgeführt. Auch hierbei wurden die Indikatorstromstärken 15 oder 30 Sekunden nach Einschalten des Indikatorstromkreises gemessen.

Auf Grund der erzielten Ergebnisse und der bestehenden Erfahrungen<sup>6,7</sup> soll der Potentialunterschied an den polarisierten Indikatorelektroden aus Kupfer mit einer Oberfläche von  $0,5 \text{ cm}^2$  in gebrauchten Lösungen von Natriumsulfat im Intervall von 50–150 mV liegen. In diesem Gebiet der Potentialdifferenz tritt ein grosser Unterschied in der Empfindlichkeit bei verschiedenen angewandten Metallen zum Vorschein, wobei sich das Indikatorsystem mit zwei polarisierten Kupferelektroden, an welchen reversible Kupferoxydation und Kupriionenreduktion stattfindet, als

bedeutend empfindlicher erwies. Durch die angegebenen Prozesse an den Kupferelektroden können auch die höhere Empfindlichkeit dieses Systems, sowie die Möglichkeit der Registrierung der Indikatorstromstärken auch bei kleiner Potentialdifferenz zwischen den Elektroden ihre Erklärung finden.<sup>8,9</sup> Abbildung 1 zeigt die Kurvenform, die Grösse der Indikatorstromstärke und die Empfindlichkeit bei Potentialdifferenzen zwischen Kupfer- bzw. Platinelektroden von 50, 100 und 150 mV mit Änderung der Konzentration der Kupriionen im Grundelektrolyten aus Natriumsulfatlösung.<sup>10</sup>

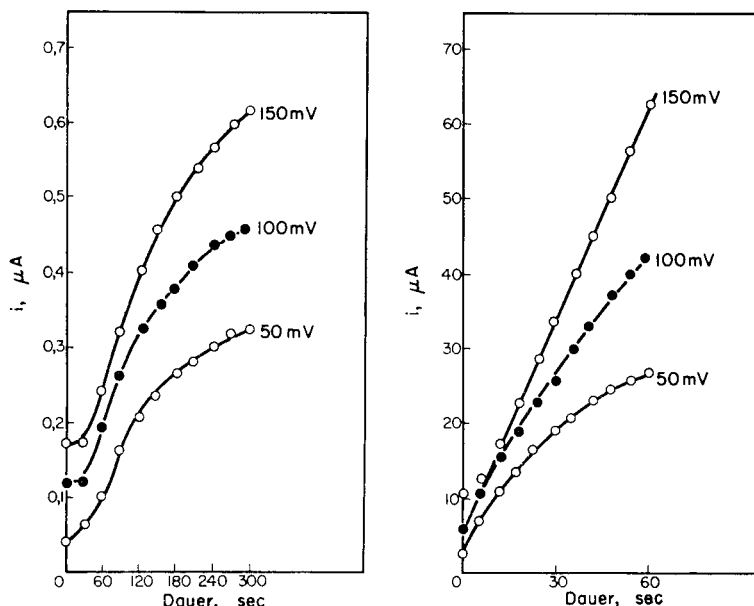


ABB. 1.—Änderung der Indikatorstromstärke mit der Änderung der Konzentration der  $\text{Cu}^{2+}$  Ionen.

Anolyt: 40 ml 0,05M  $\text{Na}_2\text{SO}_4$

Im Generatorstromkreise  $i = 49,9$  mA (170 V)

(a) Platinelektroden,  $P_K = P_A = 0,5$  cm<sup>2</sup>

(b) Kupferelektroden,  $P_K = P_A = 0,5$  cm<sup>2</sup>.

Die Untersuchung der Änderung der Indikatorstromstärke mit der Änderung der Konzentration der Kupriionen wurden grösstenteils an Kupferelektroden kleiner Oberflächen ausgeführt, da Messungen der Indikatorstromstärken an Elektroden grösserer Oberfläche bei Generatorstromstärken grösser als 10 mA nicht genügend reproduzierbar und unzuverlässig sind, wegen der Induktion parasitärer Ströme im Indikatorstromkreise.<sup>11</sup> Das System der polarisierten Kupferelektroden von 0,5 cm<sup>2</sup> Oberfläche, aber, erlaubt mit genügend grosser Empfindlichkeit die Anwendung von Generatorstromstärken grösser als 10 mA. Unter allen Umständen sollen dabei die Indikatorelektroden ausserhalb des Stromfeldes der Generatorelektroden liegen<sup>12</sup> und ausserden soll während der Messung der Indikatorstromstärke der Generatorstrom unterbrochen werden.

#### Coulometrische kuprimetrische Bestimmung der Anthranilsäure

Die coulometrische kuprimetrische Bestimmung der Anthranilsäure wurde mit konstanter Stromstärke, beim getrennten Anolyten und Katholyten ausgeführt.<sup>12</sup>

Die Fällung der Kupriionen durch Anthranilsäure erfolgt im pH-Gebiet von 2,79 bis 7.<sup>13</sup> Amperometrische Titration der Kupferionen durch Anthranilsäure wurde bei pH der Säurelösung von 4,5 bis 5,5 unter Zugabe von Äthanol ausgeführt.<sup>14</sup>

Bei der systematischen Untersuchung des Einflusses des pH-Wertes Natriumsulfatlösung hat es sich gezeigt, dass bei pH 5 und 6 zu niedrige Resultate erhalten werden. Bei pH 5 beträgt der Fehler der Bestimmung  $-25$  bis  $-30\%$  und bei pH 5,9  $-11\%$  bis  $-13\%$ , wobei auch durch Zugabe von Äthanol keine Besserung der Ergebnisse erzielt werden konnte. Bei einem pH von 6,8 bis 7 jedoch, werden bei der metallometrischen kuprimetrischen Bestimmung des Natriumanthranilats, bzw. der Anthranilsäure, zufriedenstellende Resultate erhalten und der mittlere Fehler bei 30 bis 80 mg Anthranilsäure bewegt sich in Grenzen von  $-0,3$  bis  $0,2\%$ , wobei sich der Fehler einzelner Bestimmungen um  $\pm 0,8\%$  bewegt (Tabelle I).

TABELLE I

Dauer, sec	Genommen, mg	Gefunden, mg	Fehler	
			mg	%
489,9	34,57	34,74	0,17	0,5
484,2		34,33	-0,24	-0,7
489,6		34,72	0,15	0,4
490,5	40,09	34,78	0,21	0,6
567,0		40,21	0,12	0,3
564,0		39,99	-0,10	-0,2
751,8	53,45	53,31	-0,14	-0,3
752,4		53,35	-0,10	-0,2
760,2		53,90	0,45	0,8
969,0	69,14	68,71	-0,43	-0,6
676,2		69,22	0,08	0,1
671,4		68,88	-0,26	-0,4
1130,4	80,18	80,15	-0,02	-0,03
1132,8		80,32	0,15	0,2
1122,0		79,56	-0,62	-0,8

1,7286 gr Anthranilsäure in 1000 ml 0,05-0,1M Lösung von  $\text{Na}_2\text{SO}_4$ ; pH = 6,96.

Generatorstromkreis,  $i = 49,9$  mA,  $\sim 90$  mV,  $P_A = 12$  cm<sup>2</sup>.

Indikatorstromkreis, 50 mV an zwei polarisierten Kupferelektroden,  $P_A = P_R = 0,5$  cm<sup>2</sup>.

Die Bestimmungen der Anthranilsäure wurden meistens in 30-40 ml der 0,05-0,1M Natriumsulfatlösung mit einer Stromstärke von 49,9 mA, einer Stromdichte von 4,2 mA/cm<sup>2</sup> und mit einer Generatorstromspannung von etwa 90 V ausgeführt, aus einem elektronischen Stromstabilisator mit automatischer Stromregelung innerhalb  $\pm 0,2\%$ . Der Anolyt wird mit einem elektrolytischen Schlüssel mit dem Katholyten verbunden und während der Bestimmung gerührt. Die Zeitmessung erfolgt mit einer Stoppuhr. Im Indikatorsystem aus zwei polarisierten Kupferelektroden von einer Oberfläche von 0,5 cm<sup>2</sup>, auf die eine Potentialdifferenz im Betrage von 50 oder 100 mV gelegt ist, ändert sich die Indikatorstromstärke während einer Titration von 69,14 mg Anthranilsäure mit einer Stromstärke von 49,9 mA nach der Abb. 2.

Der horizontale Teil der Titrationskurve entspricht einer  $\text{Cu}^{2+}$  Ionenerzeugung während einer Minute der Elektrolyse. Bei Bestimmungen bei welchen im Indikatorsystem eine Potentialdifferenz von 50 mV herrscht, nach Erreichen einer Indikatorstromstärke von etwa 20  $\mu\text{A}$ , wenn der horizontale Teil der Titrationskurve zwischen 10 und 15  $\mu\text{A}$  liegt, wird die elektrolytische Erzeugung der Kupriionen in Beträgen, die einer Dauer von 15 Sekunden entsprechen, durchgeführt. Bei Bestimmungen, aber, die mit einer Potenzialdifferenz zwischen den Indikatorelektroden von 100 mV ausgeführt werden, und der horizontale Teil der Titrationskurve zwischen 15 und 25  $\mu\text{A}$  liegt, wird die Erzeugung der  $\text{Cu}^{2+}$  Ionen in Zeitabschnitten fortgesetzt. In dem Kurventeil, in welchem die elektrolytische Erzeugung der  $\text{Cu}^{2+}$  Ionen in Beträgen die der Elektrolysendauer von 2 Minuten, oder 1 Minute entsprechen, erzeugt werden, wird immer nach jeder elektrolytischen Kupriionenzugabe etwa 1 Minute abgewartet um genügend Zeit für chemische Reaktion zu geben, und erst danach

wird der Indikatorstromkreis eingeschaltet und die Messung der Indikatorstromstärke nach etwa 15 oder 30 Sekunden ausgeführt. Das Rühren des Anolyten wird während der Messung der Indikatorstromstärke nicht unterbrochen. Nach jeder Bestimmung sollen die Generatoranode und die Indikatorelektroden, in Salpetersäure gewaschen, frisch mit Kupferüberzug elektrolytisch überzogen werden.

Es hat sich auch bei dieser coulometrischen Bestimmung als nützlich (vorteilhaft) erwiesen, eine vorherige Bestimmung auszuführen und grob den Endpunkt zu bestimmen, wegen der Konstruktion des horizontalen Teiles der Titrationskurve bis zu dem, durch vorherige Bestimmung, gefundenen Zeitpunkt.

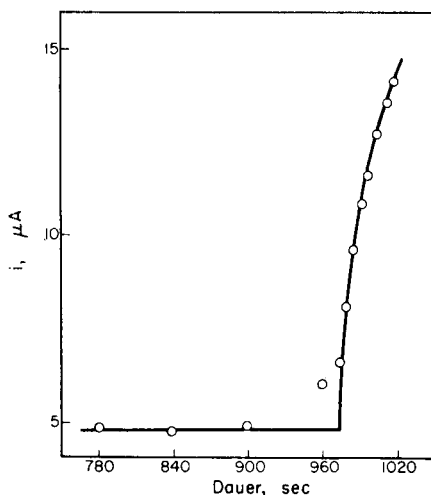


ABB. 2.—Änderung der Indikatorstromstärke während der coulometrischen Titration der Anthranilsäure.

Dauer der Bestimmung 973,5 sec

Genommen 69,14 mg

Gefunden 69,03 mg

Generatorstromkreis  $i = 49,9$  mA,  $P_A = 12$  cm<sup>2</sup>

Indikatorstromkreis mit zwei polarisierten Kupferelektroden,  $P_A = P_K = 0,5$  cm<sup>2</sup>;  
Potentialdifferenz 100 mV.

Beim starken Überschreiten des Endpunktes bekommt man unrichtige Resultate, mit einem positiven Fehler, und eine Titrationskurve veränderter Form, was wahrscheinlich durch eine Adsorption der Kupriionen an dem gebildeten Niederschlag und durch Bildung des Kuprihydroxyds erklärt werden kann.

Durch diese Untersuchung wurden die Möglichkeit und die Bedingungen für eine quantitative elektrolytische Erzeugung der Kupriionen festgelegt und darauf fussend, konnte eine neue Methode der coulometrischen Metallometrie, die coulometrische Kuprimetrie in die analytische Chemie eingeführt werden.

**Summary**—Conditions for the quantitative electrolytic dissolution of copper to yield copper(II) ions have been found, and based on this a coulometric titration of anthranilic acid with electrolytically generated copper(II) ions has been developed. The end-point is determined amperometrically with two polarized copper electrodes.

**Résumé**—On a trouvé des conditions pour la dissolution électrolytique quantitative du cuivre donnant des ions cuivre(II), et en se basant sur cela on a élaboré un titrage coulométrique de l'acide anthranilique par les ions cuivre(II) produits électrolytiquement. Le point de fin de dosage est déterminé ampérométriquement avec deux électrodes de cuivre polarisées.

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## SHORT COMMUNICATIONS

### Spectrophotometric study of the mercury(II)-Xylenol Orange chelate

(Received 28 June 1967. Revised 10 January 1969. Accepted 31 January 1969)

IN 1956 Körbl and Přibil reported the synthesis of a new metal indicator designated Xylenol Orange and gave lower pH limits for reaction with various cations.<sup>1</sup> Much research has since been done on the ability of Xylenol Orange to form chelates with metal ions, and many applications as a metallochromic indicator and as a spectrophotometric reagent have appeared in the literature. Although Körbl and Přibil reported that Xylenol Orange was suitable for determining mercury(II) on the micro or macro scale, no detailed study of the conditions under which the reaction takes place has been published. This paper gives the results of such a study.

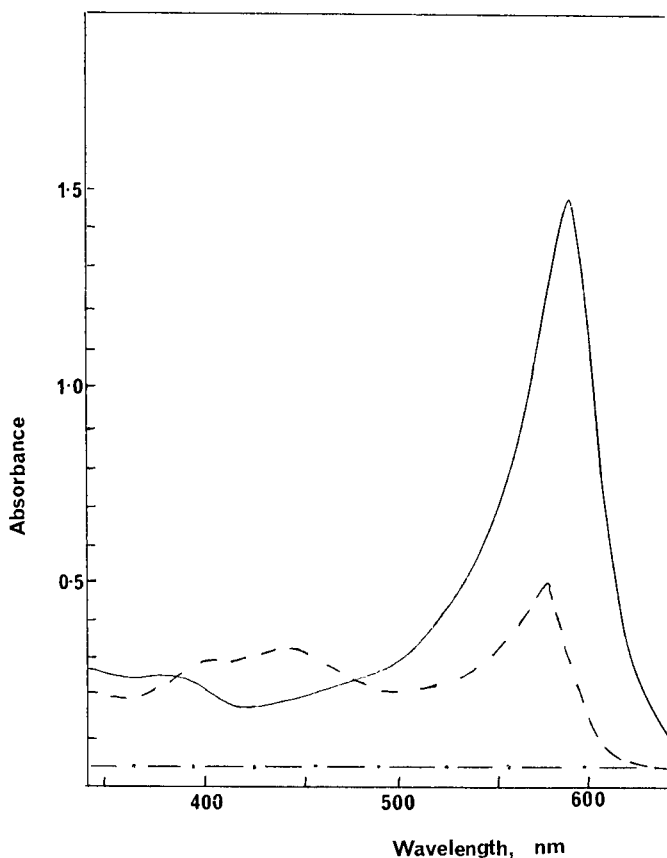


FIG. 1.—Spectrum of HMTA, Xylenol Orange and the mercury(II)-Xylenol Orange chelate at pH 7.

— · — 2.9M HMTA  
--- 5.0 × 10<sup>-5</sup>M Xylenol Orange  
—— 5.0 × 10<sup>-5</sup>M mercury(II)-Xylenol Orange chelate



## EXPERIMENTAL

Reagent grade Xylenol Orange was obtained as the tetrasodium salt and used without further purification as a  $5.0 \times 10^{-4}M$  solution prepared by dissolving 76.1 mg in distilled water and diluting to 200 ml. Mercury(II) nitrate stock solution was prepared by dissolving 983.0 mg of mercury in 25 ml of 8M nitric acid and diluting to 1 litre. A  $5.00 \times 10^{-4}M$  working solution was prepared by diluting 20.40 ml of the stock solution to 200 ml with distilled water. A saturated solution of hexamine (3.6M) was adjusted to pH 7 with nitric acid.

*Procedure*

To a 25-ml volumetric flask were added 20 ml of 3.6M hexamine and sufficient mercury(II) nitrate solution to give a final mercury concentration of  $0.5-2.0 \times 10^{-5}M$ . Then 1.0 ml of  $5.0 \times 10^{-4}M$  Xylenol Orange was added, the solution was diluted to volume with distilled water, and mixed well. The pH was  $7.0 \pm 0.1$ . The solution was allowed to stand for at least 10 min at room temperature, and then the absorbance was measured at 590 nm against a reagent blank containing only the Xylenol Orange in excess of that required for 1:1 chelate formation with the mercury(II) in the sample solution.

## RESULTS AND DISCUSSION

The absorption spectra of mercury(II)-Xylenol Orange chelate, Xylenol Orange, and hexamine solutions (pH 7) in the range 350–650 nm are shown in Fig. 1. The maxima for the chelate and Xylenol Orange solutions are at 590 and 582 m $\mu$  respectively.

Körbl and Přibil reported that the minimum pH for titrating mercury(II), with Xylenol Orange as indicator, was 5. Figure 2 shows this to be true in aqueous hexamine medium and also indicates that the maximum sensitivity is obtained at pH 7.

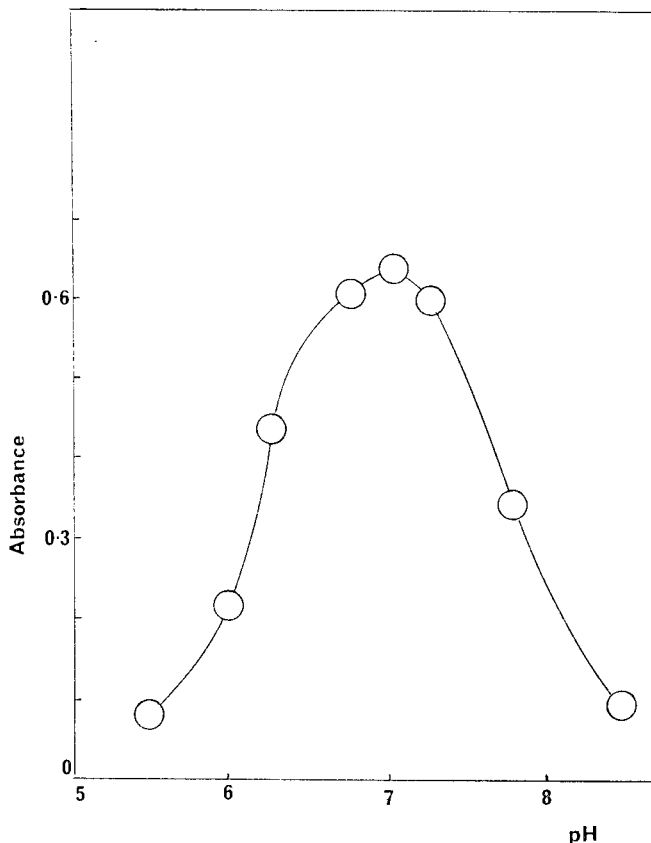


FIG. 2.—Effect of pH variation on the absorbance of the mercury(II)-Xylenol Orange chelate in 2.9M HMTA (reference solution 2.9M HMTA).

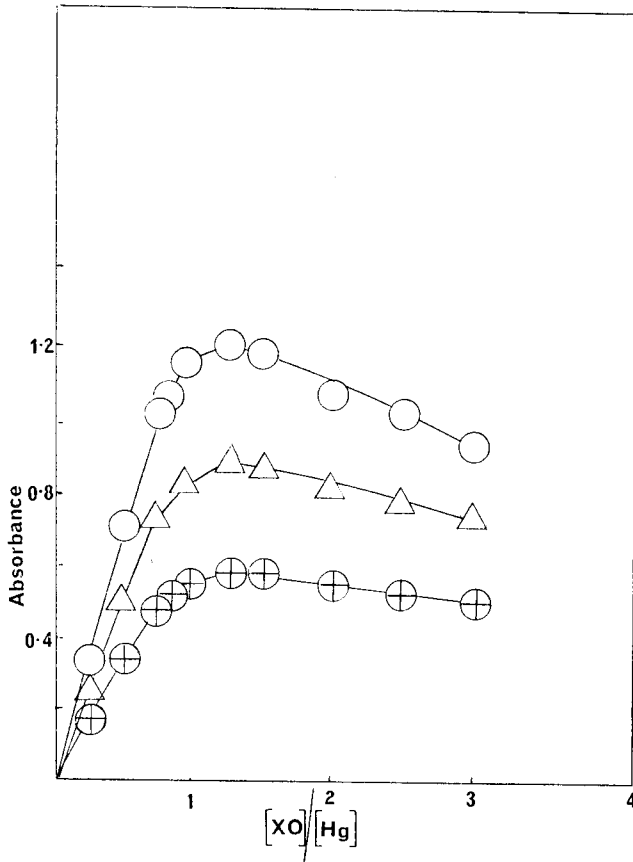


FIG. 3.—Effect of variation in the Xylenol Orange-mercury(II) molar ratio on absorbance of the chelate in 2.9M HMTA, pH 7. Reference solutions were 2.9M in HMTA and contained Xylenol Orange where necessary.

- $[\text{Hg}^{2+}] = 4.0 \times 10^{-5} M$   
 △  $[\text{Hg}^{2+}] = 3.0 \times 10^{-5} M$   
 ⊕  $[\text{Hg}^{2+}] = 2.0 \times 10^{-5} M$

Some decrease in absorbance was observed immediately after mixing, but after about 5 min the absorbance at room temperature exhibited little decrease during several hours.

When excess of Xylenol Orange is present the absorbance increases with increase in ionic strength up to 0.10M, but over the range  $\mu = 0.10\text{--}0.15M$ , the absorbance is constant and independent of ionic strength. This range can be conveniently obtained by adding an appropriate amount of ammonium nitrate to the hexamine buffer solution.

When the hexamine concentration was varied while the concentrations of mercury(II) and Xylenol Orange were held constant, there was no effect on the absorbance of solutions in which the mercury(II) was in excess, the absorbance was severely depressed at low hexamine concentrations but rose linearly with increasing hexamine concentration to essentially the value for solutions containing excess of mercury(II).

For a constant hexamine concentration of 2.9M and constant Xylenol Orange concentration, Beer's law is obeyed over the mercury(II) concentration range  $0.5\text{--}2.0 \times 10^{-5}M$  but the extrapolated calibration curve gives an intercept on the mercury-concentration axis, at zero absorbance. The linear portion of the curve was used to compute the molar absorptivity of the system— $3.1 (\pm 0.1) \times 10^4$ .

The mole-ratio and continuous variation methods were employed to determine the combining ratio of mercury(II) and Xylenol Orange in the chelate and to obtain a value for the apparent formation constant. Figures 3 and 4 show that a 1:1 chelate is formed under the experimental conditions used. The apparent formation constant was computed<sup>2,3</sup> as  $2.4 (\pm 0.6) \times 10^6$ .

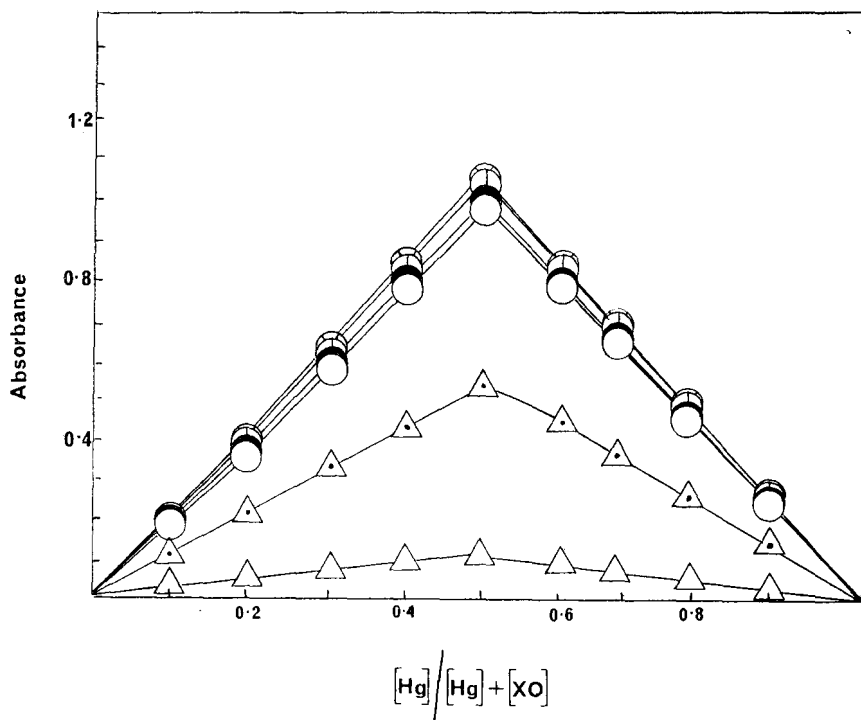


FIG. 4.—Continuous variations plot for the mercury(II)-Xylenol Orange chelate in 2.9M HMTA, pH 7. Reference solutions were 2.9M in HMTA and contained Xylenol Orange where necessary.

△ 630 nm, ▲ 550 nm, ○ 595 nm, ● 580 nm, ⊕ 585 nm, ⊗ 590 nm

The effect of hexamine concentration on the cadmium-Xylenol Orange-hexamine system was noted by Otomo<sup>4</sup> who reported that the absorbance of the system increases with the buffer concentration. Similarly for the mercury(II) system the hexamine concentration should be as high as possible to yield a linear relationship between mercury(II) concentration and absorbance. Even with 2.9M hexamine, negative deviations from Beer's law were observed for solutions containing a large molar excess of Xylenol Orange. This suggests that a single absorbing species is produced with increasing hexamine concentration when Xylenol Orange is in excess. Xylenol Orange is an EDTA analogue and therefore might be expected to form analogous metal chelates. Dwyer<sup>5</sup> considers that mercury(II) may not form a typical EDTA chelate in which the acetate groups are utilized. A paper by Přibil<sup>6</sup> suggests that for steric reasons Xylenol Orange does not form EDTA type chelates but instead forms 2:2 binuclear chelates. Thus, the nature of the synergistic effect of hexamine on the formation of the mercury(II)-Xylenol Orange chelate is not clear. It may actually enter into the chelate or perhaps exert an ionic or stereochemical influence. Certainly excess of Xylenol Orange alters the absorbing species considerably at low hexamine concentrations, but not at high, and the effect does not occur appreciably when mercury(II) is in excess.

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**Summary**—The reaction between mercury(II) and Xylenol Orange has been studied in aqueous hexamine medium. The chelate is 1:1 and has an apparent stability constant of  $2.4 (\pm 0.6) \times 10^8$  at pH 7 (2.9M hexamine). Beer's law is obeyed over the concentration range  $0.5$ – $2.0 \times 10^{-5}M$  mercury(II) when the hexamine concentration is 2.9M.

**Zusammenfassung**—Die Reaktion zwischen Quecksilber(II) und Xylenorange wurde in wäßrigem Hexamin untersucht. Es wird ein 1:1-Chelat gebildet mit der scheinbaren Bildungskonstante von  $2,4 (\pm 0,6) \cdot 10^6$  bei pH 7 (2,9M Hexamin). Das Beersche Gesetz gilt im Konzentrationsbereich  $0,5-2,0 \cdot 10^{-5}M$  Quecksilber(II), wenn die Hexaminkonzentration 2,9M ist.

**Résumé**—On a étudié la réaction entre le mercure(II) et l'Orangé Xylénol en milieu hexamine aqueuse. Le chélate est 1:1 et a une constante de stabilité moyenne de  $2,4(\pm 0,6) \times 10^6$  à pH 7 (hexamine 2,9M). La loi de Beer est suivie dans le domaine de concentrations  $0,5-2 \times 10^{-5}M$  en mercure(II) lorsque la concentration en hexamine est 2,9M.

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### Rapid spectrophotometric determination of copper in steel with zinc dibenzylidithiocarbamate

(Received 12 December 1968. Accepted 12 January 1969)

SEVERAL reagents have been proposed for the spectrophotometric determination of copper in steel, such as neocuproine,<sup>1</sup> 2,2'-biquinolyl,<sup>2</sup> oxalyl dihydrazide-acetaldehyde,<sup>3,4</sup> and substituted dithiocarbamates.<sup>5,6</sup> Turbidity is sometimes encountered with neocuproine, and 2,2'-biquinolyl is very sensitive to iron concentration. Preparation of the acetaldehyde solution is complicated by its low boiling point and evolution of heat during dilution, and the reagents have to be added quickly to prevent unwanted hydrolysis.

Zinc dibenzylidithiocarbamate (ZDBDT) has been used for determining small amounts of copper in dyes and rubber chemicals,<sup>7</sup> drinking water,<sup>8</sup> and boiler feed water.<sup>9</sup> A fairly acidic medium is used, which keeps the copper in solution and prevents hydrolysis or precipitation of other constituents. The sensitivity and simplicity, coupled with the advantage of using fairly acidic solution, suggested the exploration of ZDBDT for determining copper in plain and low- and high-alloy steels.

## EXPERIMENTAL

*Reagents*

All reagents should be of analytical-reagent grade, and water should be demineralized and distilled.

*Mixed acids.* Cautiously and slowly add 150 ml of conc. sulphuric acid to 300 ml of water, cool, and add 150 ml of conc. phosphoric acid. Dilute to a litre with water.

*Standard copper solution.* Dissolve 1.000 g of electrolytic grade copper in 10 ml of nitric acid (1 + 1). Gently boil off oxides of nitrogen and cool. Dilute accurately to a litre with water, mix, and dilute further 100-fold (1 ml contains 10  $\mu$ g of copper).

*Zinc dibenzylidithiocarbamate.* A 0.05% solution in carbon tetrachloride. Store in an amber glass-stoppered bottle.

*Procedure*

Weigh an appropriate sample (see below, optimum is 10–50  $\mu$ g of copper in the aliquot) into a 150-ml beaker. Add 10 ml of mixed acids, and simmer to dissolve, adding water from time to time to prevent crystallization of salts. When the reaction ceases, add a few drops of 30-volume hydrogen

peroxide to destroy the carbides. Cool somewhat, add about 10 ml of water and gently boil off the excess of peroxide. Cool and dilute with water to volume in a standard flask.

Copper, %	Sample, g	Dilution (ml)	Aliquot, ml
0.005-0.05	0.5	100	20
0.05-0.5	0.2	200	10
0.5-5.0	0.1	500	5

Take an appropriate aliquot in a 125-ml separatory funnel. Add 5 ml of 9M sulphuric acid and dilute to 50 ml with water, add 10 ml of the reagent solution and shake for 1 min. Let settle and draw off the organic extract into a dry 50-ml beaker. Extract again for 30 sec with 10 ml of reagent solution, combine the extracts and filter them through a Whatman No. 541 paper (or equivalent) into a dry 25-ml volumetric flask. Wash the filter with a little carbon tetrachloride and dilute to the mark. Measure the absorbance at 430 nm in a 10-mm cuvette against carbon tetrachloride. Run a reagent blank through the whole procedure and subtract its absorbance. Prepare a calibration curve covering the range up to 50  $\mu$ g of copper, starting in the procedure at addition of 9M sulphuric acid.

### Interferences

Martens and Githens,<sup>7</sup> and Wilson<sup>9</sup> investigated the effect of various elements, including iron, which was said not to interfere in up to 500-mg amounts.<sup>7</sup> This was confirmed; it was found that 200 mg of spectrographically pure iron gave a net absorbance of 0.011 in 25 ml of carbon tetrachloride when extracted directly. The interference due to 100 mg of iron (the maximum present when the largest sample weight is used) corresponds to less than 0.001% of copper. If the effect of iron is attributed to copper impurity, the iron used would contain  $\sim$ 6 ppm of copper. A similar study made with "Ferrovac E" (commercially available 99.95% Fe) indicated the presence of 0.002% copper (20 ppm); spectrographic examination of the Ferrovac E showed the presence of not more than 0.004% copper.

Martens and Githens<sup>7</sup> reported that cobalt and nickel do not interfere, and this was confirmed for amounts equivalent to those that would be derived from, *e.g.*, permanent magnet alloys (Ni 13%, Co 23%).

Bismuth gives a complex which absorbs at 435 nm, and interferes; some steels (*e.g.*, a U.S. Steel Corp. free-machining steel) contain bismuth. Martens and Githens have proposed a method for eliminating bismuth interference.<sup>7</sup>

## RESULTS AND DISCUSSION

The procedure described for the determination of copper was applied to a variety of steels and the results are recorded in Table I. The accuracy and precision are satisfactory.

The acidity needed is not critical and can range between 0.5 and 2*N*, obviating any hydrolysis or emulsion formation. The colour was verified to be stable for at least 1 hr.<sup>10</sup> The range of the method

TABLE I.—DETERMINATION OF COPPER IN STANDARD STEEL SAMPLES

Sample	Copper found, %			Standard deviation, %	Certificate value, copper, %
NBS 8i (Bessemer)	0.017	0.016	0.016	0.001	0.016
NBS 15f (B.O.H.)	0.087	0.089	0.085	0.002	0.086
	0.086				
NBS 106a* (Cr-Mo-Al steel)	0.149	0.149	0.151	0.001	0.156
NBS 32e† (Cr-Ni steel)	0.126	0.125	0.125	0.001	0.127
BCS (Mild steel)	0.206	0.208	0.202	0.006	0.20
	0.205	0.218			
BCS 326 (Mild steel)	0.367	0.352	0.352	0.007	0.36
	0.365				
BCS 266‡ (Permanent Magnet Alloy)	3.36	3.39	3.36	0.037	3.33
	3.22	3.42			

\* (Ni 2.77% + Cr 1.15% + Mo 2% + Al 1.08%)

† (Ni 1.19% + Cr 7%)

‡ (Ni 13.3% + Co 23.4% + Al 7.95% + Nb 1.21%; Fe 49.7%)

is 0.005–5% copper. A set of 6 samples can be analysed in about an hour. The method has also been applied to determine copper in inclusions and corrosion products where the available sample amounted to less than 1 mg.

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**Summary**—A rapid spectrophotometric method employing zinc dibenzylidithiocarbamate is described for determining copper in a wide variety of steels. The acidity is not critical (0.5–2*N*) and the colour of the complex is stable for >1 hr. The range of the method is 0.005–5% copper and 6 samples can be analysed in about an hour.

**Zusammenfassung**—Eine schnelle spektrophotometrische Methode zur Bestimmung von Kupfer in vielen verschiedenen Stählen mit Zinkdibenzylidithiocarbamat wird beschrieben. Die Acidität ist nicht kritisch (0,5–2*N*) und die Farbe des Komplexes ist über eine Stunde lang stabil. Die Methode funktioniert im Bereich 0,005–5% Kupfer; 6 Proben können in etwa einer Stunde analysiert werden.

**Résumé**—On décrit une méthode spectrophotométrique rapide utilisant le dibenzylidithiocarbamate de zinc pour la détermination du cuivre dans une grande variété d'aciers. L'acidité n'est pas critique (0,5–2*N*) et la coloration du complexe est stable pendant plus d'une heure. Le domaine de la méthode est de 0,005–5% de cuivre et l'on peut analyser 6 échantillons en une heure environ.

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#### Determination of uranium in uraniferous coal

(Received 14 October 1968. Accepted 18 December 1968)

A LARGE potential low-grade reserve of uranium is contained in poor quality coals, including lignite, sub-bituminous coal and carbonaceous shale. Since the uranium is concentrated in the ash when coal is burned, there is a possibility that some of the uraniferous coal could be utilized as a commercial fuel and the uranium extracted from the ash as a by-product.

The purpose of the present work was to determine the uranium content of samples of uraniferous coal found in mines in northern Greece.

Several methods are described in the literature for the determination of small amounts of uranium in different materials. Among the methods proposed, that of neutron-activation analysis is simple and sensitive and has been used by many workers<sup>1–7</sup> for the determination of uranium in rocks and minerals. Most of the procedures are based on the study of <sup>239</sup>U or <sup>239</sup>Np or a fission product isolated

by precipitation, extraction or ion-exchange after irradiation of the samples. Most of these methods have the disadvantage that they are not quantitative, which means that a carrier must be added to obtain a yield correction for each determination, while in other methods several purification steps are necessary in order to obtain selective isolation of the desired isotope.

In the present work, extraction chromatography is used for the quantitative and selective isolation of carrier-free  $^{239}\text{Np}$ .<sup>8</sup>

## EXPERIMENTAL

### *Preparation of samples for irradiation*

Standard solutions were prepared from spectroscopically pure uranyl nitrate to give a final uranium concentration of about 50  $\mu\text{g/ml}$ .

Approximately 3-g portions of the finely ground samples were heated carefully at about 600°C for a few hours to eliminate the organic matter present. Weighed portions of the ash (about 0.25 g) were put into Teflon beakers and dissolved by digestion with a mixture of concentrated nitric and hydrofluoric acids. Traces of hydrofluoric acid were removed by evaporation and the dry residue was dissolved in a few ml of nitric acid and transferred with water into a 10-ml volumetric flask.

### *Irradiation*

Two ml each of the standard and sample solutions were put into separate polyethylene ampoules which were sealed and placed on a rack (rotated at 11 rpm) in the "Democritos" swimming pool reactor. Three aliquots of each sample and two standards were irradiated together in a thermal flux of about  $2 \times 10^{12}$  n.cm<sup>-2</sup>.sec<sup>-1</sup>, the irradiation times ranging from 2–4 hr.

### *Separation procedure*

Perricos and Thomassen's extraction procedure<sup>8</sup> was applied 12–15 hr after irradiation.

The column was 140 mm long and 6 mm in diameter (volume 4 ml) and consisted of 0.5M thenoyl-trifluoroacetone in xylene as stationary phase on grade G2 Pyrex glass powder (100–170 mesh) as support. The bed density was 1.25–1.29 g/ml and the free column volume 1.1 ml. The flow-rate was 2–3 drops/min and the mobile phase was 0.9–1.0M hydrochloric acid/0.15M hydroxylamine hydrochloride. One ml of the irradiated solution was transferred to a 100-ml beaker and treated with 5 ml of concentrated nitric acid. The solution was evaporated to dryness and 10 ml of concentrated hydrochloric acid were then added. The solution was evaporated to a volume of  $4.5 \pm 0.5$  ml and transferred to a 25-ml volumetric flask with 6.5 ml of 0.8M hydroxylamine hydrochloride. The flask was then placed for 40 min in boiling water to reduce neptunium quantitatively to the extractable neptunium(IV). After the reduction, the volumetric flask was cooled to room temperature and the solution diluted to 25 ml. One ml of the active solution was then placed on the column which was then started. When the level of the active solution reached the top of the column, 4 ml of wash-solution (0.5M hydrochloric acid/0.1M hydroxylamine hydrochloride) were added, 1–2 drops at a time. When the level of the wash-solution reached the top of the column, 2 ml of 6M hydrochloric acid were added and the eluted neptunium was collected in a counting tube. The column was washed with 2 ml of 96% ethyl alcohol and 2 ml of 6M hydrochloric acid to elute all the neptunium.

### *Radiochemical purity and counting*

The eluates of both samples and standards were counted on a gamma scintillation spectrograph [50 × 50 mm NaI(Tl) crystal] adjusted to accept the 106-keV  $\gamma$ -peak of  $^{239}\text{Np}$ . Identical geometries were maintained for both samples and standards and each solution was counted for at least 5 min. Longer counting periods were required in some cases because of the low activity level. The radiochemical purity of the separated neptunium was checked by drawing decay curves and examining the  $\gamma$ -spectra on a 400-channel analyser.

## RESULTS

In order to reduce statistical error, at least two  $^{239}\text{Np}$  samples were isolated from each irradiated standard and from each sample. The average chemical yield of the separation method for neptunium has been shown<sup>8</sup> to be 99.5%. Because the samples and standards are irradiated in dilute aqueous solutions, any variation in the neutron flux because of self-shielding<sup>9</sup> is eliminated, owing to the low absorption cross-section of water.

In order to estimate the accuracy of the method two IAEA reference samples were analysed for uranium. The results are listed in Table I. The results obtained are in good agreement with the reported values, but the mean values are about 2% higher.

TABLE I.—URANIUM CONTENT OF IAEA (VIENNA) SAMPLES

Reference sample	Present work U, %	Reported value U, %
Torbernite	0.284 0.260	0.266
Carnotite	0.376 0.345	0.355

Uranium was determined in six samples of uraniferous coal obtained from two different regions. The samples were prepared, irradiated and chemically processed as described above and the results are presented in Table II. The uranium content of the original samples is low, but is increased about fivefold in the ash.

TABLE II.—URANIUM CONTENT IN URANIFEROUS COAL

Sample	U in ash, %	U in original sample, %
U-1	0.20	0.037
U-2	0.14	0.037
U-3	0.24	0.036
U-4	0.09	0.012
U-5	0.10	0.017
U-6	0.08	0.015

The advantages of the proposed method are that no yield correction is necessary, only one purification is involved and many determinations can be made at the same time. The error is about  $\pm 5\%$ , and the time required for a complete analysis, after irradiation, is about 3 hr.

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**Summary**—The uranium content of uraniferous coal has been determined by neutron-activation analysis. Carrier-free  $^{239}\text{Np}$  is separated quantitatively and selectively by column extraction chromatography with glass powder as support and thenoyltrifluoroacetone in xylene as stationary phase. Only one purification step is involved.

**Zusammenfassung**—Der Urangehalt uranförender Kohle wurde durch Neutronenaktivierungsanalyse bestimmt. Trägerfreies  $^{239}\text{Np}$  wird quantitativ und selektiv durch Säulenextraktionschromatographie mit Glaspulver als Träger und Thenoyltrifluoracetone in Xylol als stationärer Phase abgetrennt. Man benötigt nur einen Reinigungsschritt.

**Résumé**—On a déterminé par analyse par activation de neutrons la teneur en uranium de houille uranifère. Le  $^{239}\text{Np}$  exempt d'entraîneur est séparé quantitativement et sélectivement par chromatographie d'extraction sur colonne avec pour support de la poudre de verre et pour phase stationnaire la thenoyltrifluoracétone en xylène. On ne met en jeu qu'un seul stade de purification.

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## Colorimetric determination of zirconium with 1-(2-pyridylazo)-2-naphthol

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ZIRCONIUM is one of the major fission products present in discharged reactor fuels and its recovery is of importance. Pyrochemical processes are being developed for the recovery,<sup>1,2</sup> and inactive synthetic fuels are being used to evaluate them. Determination of zirconium is necessary at the 10-ppm level in samples of magnesium-zinc metal and magnesium chloride-calcium fluoride flux and at the 100 ppm level in uranium product samples.

The colorimetric determination of zirconium with Alizarin Red-S<sup>3,4</sup> is not particularly sensitive, specific or rapid for uranium-fission element alloys. The barium fluozirconate precipitation that is required to separate zirconium from interfering ions such as rhodium, ruthenium and molybdenum precludes the use of these procedures with samples which contain magnesium or calcium. The spectrophotometric method based on Xylenol Orange<sup>5</sup> has the desired sensitivity, but other fission elements interfere; the absorbance of the zirconium-Xylenol Orange complex is very acid-dependent and the wavelength of the maximum absorbance increases with increasing zirconium concentration.

Rolf<sup>6</sup> has described a method for the determination of zirconium with 1-(2-pyridylazo)-2-naphthol (PAN) as the chromogenic reagent. Zirconium is separated from interferences by repeated extractions with chloroform-dibutyl phosphate (HDBP), the organic phases are filtered to remove entrained droplets of the aqueous phase, and the colour is developed in the organic phase. The method is rapid, sensitive, and relatively free from interference. The method, when compared with other zirconium colorimetric methods, has the particular advantage of tolerating mg-amounts of fluoride. This is of great importance when it is considered that fluoride is the most effective reagent for the dissolution of zirconium-bearing alloys.

In evaluation of Rolf's method for the analysis of the solutions of salts and alloys discussed above, several problems were encountered. The results obtained with standard zirconium solution were low and erratic, uranium interfered when the uranium: zirconium ratio was >20, and the procedure was not applicable to solutions where the zirconium concentration was less than 2 µg/ml.

In the method described here, these problems have been overcome. By use of toluene rather than chloroform as a diluent for dibutyl phosphate only a single extraction is needed and there is no entrainment of aqueous phase; the organic phase can be easily scrubbed to remove uranium, and a simple procedure has been devised for concentrating µg-quantities of zirconium from large volumes of solution.

## EXPERIMENTAL

*Cylindrical 25-ml separatory funnels, with Teflon stopcocks.*

### Reagents

*m-Cresol Purple*, 0.1% aqueous solution. To aid in dissolution of the dye, add a few drops of ammonia solution.

*Fluoboric acid*, 5% v/v solution.

*Aluminium nitrate solution*. Dissolve 2.25 kg of aluminium nitrate nonahydrate in 1160 ml of water. Heat to incipient boiling. While stirring, add 1% potassium permanganate solution dropwise until a pink colour persists for 1-2 min. The solution becomes pale yellow on standing. Cool, and add 121 ml of concentrated nitric acid.

*Pyridine*. Fresh or redistilled.

*Di-n-butyl phosphate (HDBP)*,  $2.3 \times 10^{-3}M$ . Dilute 0.50 ml to 1 l. with toluene. (The purification procedure described by Rolf<sup>6</sup> was unnecessary with the material used by us.)

*1-(2-Pyridylazo)-2-naphthol (PAN)*, 0.05% in methanol. Mix 91 ml of pyridine, 228 ml of 0.05% PAN solution and dilute to 1 l. with toluene.

**Zirconium solutions, 5-6 mg/ml.** Dissolve 1.1 g of zirconyl chloride (hafnium-free) in dilute hydrochloric acid. Add sufficient concentrated hydrochloric acid to make the 100-ml final volume 6M in acid. Standardize this solution by titration with EDTA.<sup>7</sup> Prepare working solutions by appropriate dilution.

**Ammonium thiocyanate, 10% solution.**

**Zirconium tracer, <sup>95</sup>Zr-<sup>95</sup>Nb solution.** The niobium daughter was separated by the method of Larsen *et al.*<sup>3</sup> A radiochemical analysis for zirconium established that the tracer contained only zirconium-95.

#### Procedure

Transfer an aliquot, containing 10-80  $\mu\text{g}$  of zirconium, into a 25-ml separatory funnel containing 1 ml of 5% fluoboric acid solution. Add 2 drops of *m*-Cresol Purple indicator and then 7M aqueous ammonia dropwise until the colour changes to yellow. Dilute to 5 ml, add 12.5 ml of the aluminium nitrate solution and exactly 5 ml of  $2.3 \times 10^{-3}M$  HDBP. Shake for 30 sec, allow the phases to separate and drain off the aqueous phase. (If U:Zr is  $>20$ , scrub the organic phase by shaking it for 1 min with 5 ml of 0.5M hydrochloric acid and 1 ml of 10% ammonium thiocyanate solution; repeat if  $>40$  mg of uranium are present.) Transfer exactly 3 ml of the organic phase to a 25-ml volumetric flask. Dilute to volume with the PAN solution, mixing during the addition. Let stand 1 hr for colour development. Measure the absorbance at 555 nm in 10-mm cells *vs.* a blank carried through the entire procedure. Calibrate as usual.

Beer's law is obeyed over the concentration range 10-80  $\mu\text{g}$  of zirconium per 25 ml. The molar absorptivity is  $3.6 \times 10^4$ . The colour is stable for at least 64 hr.

Samples which require an aliquot as large as 15 ml may be concentrated by precipitation of zirconium hydroxide with an ammonia-ammonium chloride, buffer, pH 10, and 10 mg of uranium as carrier. The precipitate is centrifuged, washed with water, dissolved in 1 ml of 5% fluoboric acid solution and a few drops of 3M nitric acid, then carried through the procedure.

#### DISCUSSION

Rolf's<sup>6</sup> procedure was found to give somewhat erratic results because of adsorption of up to 25% of the zirconium on the cotton used to remove aqueous droplets from the chloroform. Glass wool gave comparable results. When the filtration was omitted, the blanks were high and variable. When toluene was substituted for chloroform, the difficulties disappeared, zirconium was completely removed in one extraction, and no water was entrained.

The necessary concentration range of HDBP was found to be  $1-3.8 \times 10^{-3}M$ . Below  $1 \times 10^{-3}M$  the extraction was incomplete; above  $15 \times 10^{-3}M$  an emulsion was formed. Somewhat unexpectedly, however, the concentration of HDBP affected the colour development. When the HDBP concentration exceeded  $3.8 \times 10^{-3}M$ , colour development was appreciably slower or incomplete. This concentration of HDBP corresponds to a 1.1:1 mole-ratio of HDBP: PAN in the final solution. At a mole-ratio of 3.4:1 colour development was not complete even after 18 hr.

The amount of PAN present was more than the 14-fold molar excess found necessary by Rolf.<sup>6</sup> The amount of zirconium extracted varied from 40 to 100% with different batches of aluminium nitrate. Because the presence of some organic material was suspected, the aluminium nitrate was heated with a slight excess of potassium permanganate. This eliminated the difficulty.

TABLE I.—RECOVERY OF ZIRCONIUM (21  $\mu\text{g}$ ) IN PRESENCE OF URANIUM

U, mg	Zr recovery, %		
	1 Scrub	2 Scrubs	3 Scrubs
0	101	102	—
40	99	—	—
400	112	105	103
1000	—	99	100

Of the uranium-fission elements uranium, molybdenum, ruthenium, palladium and rhodium, only uranium interferes. Approximately 4% of the uranium is co-extracted; it is removed by scrubbing with ammonium thiocyanate-hydrochloric acid solution, but not with hydrochloric acid alone. Zirconium is not affected by the scrub solution. The results in Table I show only one scrub is needed for U:Zr  $< 200$ . When the ratio is 50000, three scrubs are necessary.

The procedure has proven to be most useful and satisfactory for the determination of 0.05%-3%

zirconium in uranium-fission element alloys and as little as 0.006% zirconium in zinc-magnesium uranium-fission element alloys. The relative standard deviation from the mean for a number of samples and standards is 2%.

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**Summary**—A method is described for the determination of as little as 50 ppm of zirconium in uranium-fission element alloys and zinc-magnesium-uranium-fission element alloys. Zirconium is extracted from a nitric acid-aluminium nitrate medium with dibutyl phosphate in toluene. The uranium co-extracted with the zirconium is removed by scrubbing with hydrochloric acid-ammonium thiocyanate solution. A portion of the organic phase is mixed with pyridine-toluene solution of 1-(2-pyridylazo)-2-naphthol to develop the colour.

**Résumé**—On décrit une méthode pour la détermination de quantités de zirconium aussi petites que 50 ppm dans les alliages d'éléments de fission de l'uranium et les alliages zinc-magnésium-éléments de fission de l'uranium. On extrait le zirconium d'un milieu acide nitrique-nitrate d'aluminium par éliminé par lavage avec une solution acide chlorhydrique-thiocyanate d'ammonium. On mélange une fraction de la phase organique avec une solution en pyridine-toluène de 1-(2-pyridylazo)2-naphtol pour développer la coloration.

**Zusammenfassung**—Ein Verfahren zur Bestimmung von 50 ppm Zirkonium in Legierungen aus Uran und Spaltelementen und aus Zink, Magnesium, Uran und Spaltelementen wird beschrieben. Zirkonium wird mit Dibutylphosphat in Toluol aus einem Medium aus Salpetersäure und Aluminiumnitrat extrahiert. Das mit dem Zirkonium extrahierte Uran wird durch Waschen mit salzsaurer Ammoniumrhodanidlösung entfernt. Ein Teil der organischen Phase wird zur Entwicklung der Farbe mit einer Lösung von 1-(2-Pyridylazo)-2-naphthol in Pyridin-Toluol gemischt.

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### Potentiometric determination of iron with DTPA in the presence of a large amount of aluminium

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THE first direct potentiometric determination of iron with EDTA was proposed by Přibil, Koudela and Matyska.<sup>1</sup> Various bimetallic electrode systems have been proposed for the titration,<sup>2,3</sup> and so has biamperometric titration with two platinum or carbon electrodes.<sup>4-6</sup>

Visual complexometric determination of iron in the presence of aluminium with use of various indicators is the subject of a great number of publications. Because of the great difference in stability constants between the iron and aluminium EDTA complexes no difficulties should occur in the determination of iron in the presence of a moderate amount of aluminium, but reliable results are obtained only if the Al:Fe ratio is not too large. Although the stability constant of the aluminium DTPA complex (DTPA = diethylenetriaminepenta-acidic acid) is not known, preliminary experiments showed that aluminium is more easily displaced from its DTPA complex than from its EDTA complex. Therefore iron may be determined by direct titration with DTPA in the presence of a large amount of aluminium. We obtained very good results for iron up to an Al:Fe ratio of 70, at which good results cannot be reached by visual titration.

Aluminium can be determined, after addition of a complexone, by back-titration with iron(III). DCTA is more convenient for this determination than is EDTA, because aluminium forms the DCTA complex immediately and is not displaced from it during the back-titration.

## EXPERIMENTAL

### Reagents

*DTPA, 0.05M*, prepared by dissolving 19.67 g of the free acid (Geigy) by heating in 130–150 ml of 1M sodium hydroxide, cooling after dissolution, and diluting to 1 litre; standardized by potentiometric titration with iron(III) chloride.

*DCTA, 0.05M*, prepared by dissolving 17.73 g of the free acid in the same way, and standardized with iron(III) chloride.

*Buffer solution, pH 1.6*; 94.5 g of monochloroacetic acid and 3.6 g of sodium hydroxide dissolved in 1 litre of distilled water.

*Buffer solution, pH 5.0*; 280 g of sodium acetate trihydrate dissolved in 500 ml of distilled water, 50 ml of glacial acetic acid added, and the whole diluted to 1 litre.

*Iron(III) chloride, 0.05M*; prepared from the reagent grade chemical and standardized gravimetrically.

### Procedure

To a slightly acid sample solution add 5 ml of buffer (pH 1.6) and dilute to 100 ml. Titrate with 0.05M DTPA until the potential break is reached. The DTPA used corresponds to iron. Add a known amount of DCTA (more than equivalent to the aluminium present), 15 ml of buffer solution (pH 5) and titrate the excess of DCTA with 0.05M iron(III) chloride. A correction must be applied for the small excess of DTPA added after the first end-point was reached.

TABLE I.—DETERMINATION OF IRON IN THE PRESENCE OF A LARGE AMOUNT OF ALUMINIUM

Taken		Found	
Fe, mg	Al, mg	Fe, mg	Al, mg
13.96	6.75	13.9 <sub>6</sub>	6.68
13.96	20.25	13.9 <sub>6</sub>	20.1 <sub>2</sub>
13.96	67.5	13.8 <sub>2</sub>	67.5
13.96	270	14.2 <sub>4</sub>	267
13.96	675	13.9 <sub>6</sub>	672
13.96	1012	13.8 <sub>2</sub>	1012

## RESULTS

Typical results are summarized in Table I. This method gives reliable results up to a 70:1 Al:Fe ratio, but at this extreme concentration ratio it is necessary to determine aluminium on a separate smaller portion of sample containing not more than 25 mg of aluminium.

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**Summary**—Potentiometric determination of iron with DTPA at pH 1.6 (platinum and calomel electrodes) permits determination of iron in the presence of aluminium up to an Al:Fe ratio of 70. Aluminium is determined indirectly by addition of excess of DCTA, adjustment to pH 5, and back-titration with iron(III) chloride.

**Zusammenfassung**—Die potentiometrische Methode mit DTPA bei pH 1,6 (Platin- und Kalomelelektroden) erlaubt die Bestimmung von Eisen in Gegenwart von Aluminium bis zu einem Al:Fe-Verhältnis von 70. Aluminium wird indirekt durch Zugabe von überschüssigem DCTA, Einstellung auf pH 5 und Rücktitration mit Eisen(III) chlorid bestimmt.

**Résumé**—Le dosage potentiométrique du fer au moyen de DTPA à pH 1,6 (électrodes en platine et calomel) permet de déterminer le fer en la présence d'aluminium jusqu'à un rapport Al:Fe de 70. On dose l'aluminium indirectement par addition d'excès de DCTA, ajustage à pH 5 et titrage en retour avec le chlorure de fer(III).

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### Separation and solvent extraction of vanadium and uranium with n-propyl 2,3,4-trihydroxybenzoate

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A SIMPLE procedure for the separation and spectrophotometric determination of vanadium and uranium in mixtures would compare favourably in time, effort and chemicals needed, with the existing gravimetric,<sup>1</sup> volumetric,<sup>2</sup> photometric,<sup>3-8</sup> and electrometric methods.<sup>9-11</sup> A literature survey shows that although a large number of reagents has been introduced for the determination of vanadium and uranium individually or in mixtures, most of the procedures based on them are time-consuming, almost none exploiting the selectivity and versatility of the reagents.

The present paper describes the use of n-propyl 2,3,4-trihydroxybenzoate (PTB) for the determination of both vanadium and uranium by means of a single separation. The reaction of the free acid with vanadium and uranium has been previously described<sup>12</sup> but not utilized for their determination. The ester was preferred in this work because its solutions are more stable on storage.

#### EXPERIMENTAL

##### Reagents

All reagents were analytical grade. A 4% w/v solution of PTB was prepared in t-pentanol. Lower concentrations were prepared by proper dilution with the solvent and were stable for at least two weeks. A 2% w/v solution of PTB in acetone-water medium (1:1) was prepared by dissolving the reagent in acetone and diluting with water. This solution was stable for at least one week.

Vanadium(IV) and (V) stock solutions containing 5–150  $\mu\text{g}$  of the metal per ml were prepared by dissolving the calculated amount of sodium metavanadate or vanadyl chloride dihydrate in 10 ml of 0.1M hydrochloric acid and diluting to 100 ml with water. Uranium stock solutions containing 20–300  $\mu\text{g}$  of uranium(VI) per ml were prepared by dissolving the appropriate amount of uranyl nitrate hexahydrate in 10 ml of 0.1M hydrochloric acid and diluting to 100 ml with water.

Citric acid-phosphate buffer solutions were prepared (604.5 ml of 0.2M disodium phosphate and 395.5 ml of 0.1M citric acid for pH 6.5; 972.5 ml of the phosphate and 27.5 ml of the citric acid solutions for pH 8.2), standardized, and stored in polythene bottles. Other buffers used were 5% w/v sodium sulphite and 5% w/v sodium acetate aqueous solutions.

Equal volumes of 5% w/v ammonium carbonate and 10% v/v hydrogen peroxide solutions were mixed and used as the oxidizing mixture.

#### Procedure

Transfer a neutral sample containing up to 120  $\mu\text{g}$  of vanadium and 25–275  $\mu\text{g}$  of uranium into a small separating funnel. Add 5 ml of citric acid–phosphate buffer pH 6.5, and 2 ml of 2M sodium chloride. Extract vanadium by vigorous shaking for 2 min each time with four 5-ml portions of 4% PTB in *t*-pentanol and finally with 5 ml of the pure solvent. Combine the PTB extracts and filter through a Whatman No. 30 filter paper holding about 2 g of anhydrous sodium sulphate; collect the filtrate in a 25-ml volumetric flask and wash the paper and contents with the 5 ml of solvent used for the last extraction. Dilute to the mark with solvent. Measure the absorbance at 585 nm in 10-mm silica cells against a blank solution similarly prepared.

Transfer the residual aqueous phase to a 30-ml Kjeldahl flask and adjust the pH to 8.2–8.5 with 5% sodium sulphite or 5% sodium acetate solution. Add 2 ml of 2% PTB in acetone–water (1:1) and boil the solution for 2–3 min to get rid of all the acetone present. Cool under the tap, transfer the solution into a 10-ml volumetric flask and dilute to volume with water. Measure the absorbance at 375 nm against a reagent that has been treated according to the procedure.

### RESULTS AND DISCUSSION

Preliminary investigations showed that when a slightly acidic solution, pH 6.5, of vanadium was treated with PTB dissolved in organic solvent an immediate deep blue colour appeared. The coloured complex was stable for several weeks and the colour was very reproducible. The blue species was extractable by *t*-pentanol, isopentanol, pentyl acetate, ethyl acetate, isobutanol, or isobutyl methyl ketone. The first solvent was the most efficient.

Uranyl ion solutions subjected to similar treatment were not extracted with PTB in *t*-pentanol but remained in the aqueous layer. If, however, the latter was further treated with PTB in acetone–water solution and adjusted to pH 7.6–8.8 with citric acid–phosphate buffer and sodium sulphite or acetate solution, a brown-red colour developed and reached maximum intensity on boiling for a few minutes.

The absorption spectra of the complexes are shown in Figs. 1 and 2. The blue species shows a pronounced maximum at 585 nm, and the brown-red species exhibits a maximum at 370–380 nm. At these wavelengths Beer's law is obeyed by the two systems, up to 120  $\mu\text{g}$  of vanadium in *t*-pentanol medium, 150  $\mu\text{g}$  of vanadium in aqueous acetone, and up to 275  $\mu\text{g}$  of uranium.

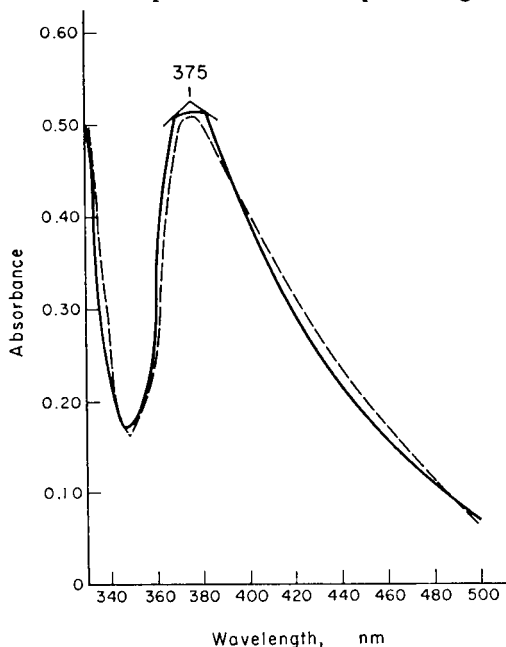


FIG. 1.—Absorption spectra of vanadium-PTB complex at 20°. — in *t*-pentanol; --- in acetone-water.

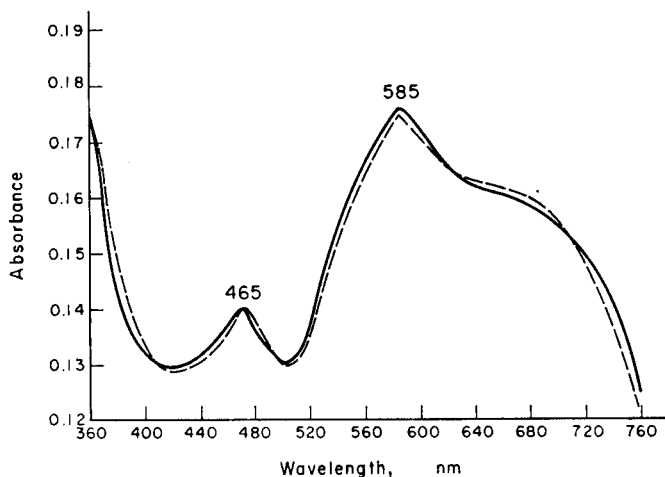


FIG. 2.—Absorption spectra of uranium-PTB complex at 20°. — in acetone-water; --- in *t*-pentanol.

The pH range over which colour intensity is constant is 4.0–8.5 for vanadium and 7.6–8.8 for uranium. PTB solutions themselves become yellow, brown or red in highly alkaline or highly acidic media. The colour is maximal and stable over the temperature ranges 15–35° and 15–90° (vanadium complex in aqueous and organic phases respectively) and 75–90° and 15–35° (uranium complex in aqueous and organic phases respectively). The colour is stable for at least 6 days, in diffuse light.

The optimum PTB concentration was found by varying it while other variables were kept constant; the volume of PTB solution added was kept constant (10 ml for vanadium, 2 ml for uranium). The permissible ranges are 0.3–5% in *t*-pentanol for vanadium, and 0.1–2% in acetone-water medium for uranium.

#### Interferences

The effects of various ions were studied by measuring the absorbance of solutions of the ions in the presence and absence of 40  $\mu\text{g}$  of vanadium and uranium. The results are shown in Tables I and II.

TABLE I.—EFFECTS OF DIVERSE IONS ON THE DETERMINATION OF VANADIUM (40  $\mu\text{g}$ )

Ion added	Amount, $\mu\text{g}$	Absorbance in absence of V	V found, $\mu\text{g}$
Uranium(VI)	500	0.000	40.0
Ruthenium(III)	100	0.100	50.8
Osmium(IV)	100	0.080	49.5
Gold(III)	100	0.040	45.0
Iron(III)	50	0.200	70.8
Lanthanum(III)	100	0.005	41.5
Copper(II)	100	0.075	48.0
Tin(II)	50	0.120	50.0
Chromium(III)	50	0.100	51.0
Chromium(IV)	50	0.080	50.0
Sodium	20000	0.000	40.0
Calcium	10000	0.000	40.0
Boron	10000	0.000	40.0
Titanium(II)	100	0.005	41.5
Titanium(IV)	100	0.005	41.5
Niobium(V)	100	0.005	42.0
Tantalum(V)	100	0.000	40.0
Cerium(IV)	100	0.005	41.5
Chloride	20000	0.000	40.0
Sulphate	10000	0.000	40.0
Citrate	10000	0.000	40.0
Phosphate	20000	0.000	40.0

TABLE II.—EFFECTS OF DIVERSE IONS ON THE DETERMINATION OF URANIUM (40  $\mu\text{g}$ )

Ion added	Amount, $\mu\text{g}$	Absorbance in absence of U	U found, $\mu\text{g}$
Vanadium(V)	500	0.000	40.0
Vanadium(IV)	500	0.000	40.0
Molybdenum(VI)	100	0.050	80.0
Iridium(IV)	100	0.004	41.5
Palladium(II)	100	0.005	42.8
Manganese(II)	100	0.004	41.5
Rhodium(IV)	100	0.001	41.0
Cobalt(II)	100	0.001	41.0
Beryllium	100	0.001	41.0
Titanium(III)	100	0.055	81.0
Titanium(IV)	100	0.055	81.0
Niobium(V)	50	0.060	85.0
Tantalum(V)	100	0.001	41.0
Sodium	20000	0.000	40.0
Calcium	10000	0.000	40.0
Chloride	20000	0.000	40.0
Phosphate	20000	0.000	40.0

\* No interference by large excess.

#### Precision and accuracy

The precision of the method was determined at two concentrations of each of vanadium and uranium. The relative standard deviation was 0.5% for vanadium and 4% for uranium, at the 50 and 100  $\mu\text{g}/\text{ml}$  levels.

Synthetic mixtures of vanadium and uranium were analysed to determine the accuracy of the method (Table III). *no significant bias was found*

#### Composition of the complexes

The continuous variations and mole-ratio methods used at two wavelengths showed that there is only one complex formed, with a ligand-to-metal ratio of 1:1 for vanadium and 2:1 for uranium. Since the blue species obtained from equimolar concentrations of vanadium(IV) and vanadium(V) absorb at the same wavelength and to the same extent, and it is known that vanadium(V) is readily reduced by organic reagents,<sup>13</sup> it is proposed that the vanadium chelate is  $\text{VO}(\text{C}_{10}\text{H}_{10}\text{O}_5)$  and the uranyl complex  $\text{UO}_2(\text{C}_{10}\text{H}_{11}\text{O}_5)_2^{2-}$ .

The stability constants were determined in the usual way and found to be  $2.10 \times 10^4$  for vanadium (12 determinations) and  $1.90 \times 10^8$  for uranium (15 determinations).

#### Procedure for phosphate rock

Weigh 1.000 g of the powdered rock into a large platinum crucible. To wet all the powder add 3 ml of water and 5 ml of concentrated nitric acid and stir. Evaporate the mixture to dryness on a steam-bath, add 5 ml of concentrated nitric acid and again evaporate to dryness. Cool, add 20 ml of water, boil for 2 min, and filter through a small paper to get rid of silica. Wash the paper with two 5-ml portions of boiling water. Pour the filtrate and washings into 10 ml of the ammonium carbonate-hydrogen peroxide oxidizing reagent and heat gently. Iron and calcium precipitate, while vanadium and uranium are converted into the water-soluble vanadate and uranyl carbonate respectively. Filter off the precipitate, dissolve it in the minimum amount of 1M hydrochloric acid and repeat the treatment with the oxidizing reagent, and filter. Make the combined filtrates and washings just acidic with 0.1M hydrochloric acid, boil for 2 min to decompose peroxide and remove carbon dioxide and cool. Dilute to volume in a standard flask and apply the described procedure to a suitable aliquot.

Synthetic 1-g samples of similar composition to native phosphate rocks and containing 25–35 ppm of each of vanadium(V) and uranium(VI) were examined. The recoveries were reproducible within  $\pm 1 \mu\text{g}$  for vanadium and  $\pm 3 \mu\text{g}$  for uranium. Similar reproducibilities were obtained with native rock samples.

*Acknowledgement*—The author wishes to express his gratitude to Mr. Ismail M. Al-Dhaher of this department for helping in part of the experimental work.

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**Summary**—A spectrophotometric method is described for the separation and determination of trace quantities of vanadium(IV) and (V) from uranium(VI). Vanadium is selectively separated from uranium by extraction at pH 6.5 into *n*-propyl 2,3,4-trihydroxybenzoate (PTB) dissolved in *t*-pentanol. Up to 120  $\mu\text{g}$  of vanadium can be determined by measuring the absorbance of the blue complex in the organic phase at 585 nm. Uranium(VI) remains in the aqueous layer and can be determined spectrophotometrically by its reaction with PTB in aqueous acetone to produce a brown-red colour at pH 7.6–8.8. Solutions containing 25–275  $\mu\text{g}$  of uranium absorb at 370–380 nm according to Beer's law. By modification, this procedure can be used for the determination of the two metals in native phosphate rocks. The effects of diverse ions on the determination of vanadium and uranium have also been examined.

**Zusammenfassung**—Ein spektrophotometrisches Verfahren zur Abtrennung von Spuren Vanadium(IV) und –(V) von Uran(VI) und zu ihrer Bestimmung wird beschrieben. Vanadium wird selektiv von Uran getrennt durch Extraktion bei pH 6,5 in *n*-Propyl-2,3,4-trihydroxybenzoat (PTB), das in *t*-Pentanol gelöst ist. Bis herauf zu 120  $\mu\text{g}$  Vanadium können durch Messung der Extinktion des blauen Komplexes in der organischen Phase bei 585 nm bestimmt werden. Uran(VI) bleibt in der wäßrigen Schicht und kann spektrophotometrisch mit Hilfe seiner Reaktion mit PTB in wäßrigen Aceton bestimmt werden: bei pH 7,6–8,8 bildet sich eine braunrote Farbe. Lösungen mit 25–275  $\mu\text{g}$  Uran absorbieren bei 370–380 nm dem Beerschen Gesetz entsprechend. Abgeändert kann dieses Verfahren zur Bestimmung der beiden Metalle in anstehenden Phosphatgesteinen dienen. Auch der Einfluß verschiedener Ionen auf die Bestimmung von Vanadium und Uran wurde untersucht.

**Résumé**—On décrit une méthode spectrophotométrique pour la séparation et le dosage de traces de vanadium(IV) et (V) de l'uranium(VI). On sépare sélectivement le vanadium de l'uranium par extraction à pH 6,5 en 2,3,4-trihydroxybenzoate de *n*-propyle (PTB) dissous en *t*-pentanol. On peut déterminer jusqu'à 120  $\mu\text{g}$  de vanadium par mesure l'absorption du complexe bleu dans la phase organique à 585 nm. L'uranium(VI) reste dans la couche aqueuse et peut être dosé spectrophotométriquement par sa réaction avec le PTB en acétone aqueuse, produisant une coloration brun-rouge à pH 7,6–8,8. Les solutions contenant 25–275  $\mu\text{g}$  d'uranium absorbent à 370–380 nm et suivent la loi de Beer. Par modification, on peut utiliser cette technique pour le dosage des deux métaux dans les roches au phosphate naturelles. On a aussi examiné les influences de divers ions sur le dosage du vanadium et de l'uranium.

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**Summary**—Digital computers are currently applied to a wide range of chemical problems. Aspects of particular interest to analytical chemists, including statistical treatment, X-ray analysis, spectroscopy, mass spectrometry, gas chromatography and electroanalytical chemistry, are discussed.

**Precipitation from homogeneous solution of cations released from EDTA complexes:** R. GRZESKOWIAK and T. A. TURNER, *Talanta*, 1969, **16**, 649. (Department of Chemistry, Woolwich Polytechnic, London, S.E.18, U.K.)

**Summary**—The suitability of EDTA complexes for use in precipitation of certain cations from homogeneous solution under various experimental conditions can be predicted from a knowledge of the solubility product of the compound to be precipitated and the complex stability constant. A brief review of previous work in the field of masking effectiveness is given. An examination of factors influencing precipitation has been carried out. It is shown that a simple ratio can be used for predicting the likelihood of precipitation at various pH values and that more rigorous theoretical approaches are not necessarily more advantageous.

**Grundlagen der Gradient-Dünnschicht-Chromatographie auf "sauerbasischen" Kieselgel-Schichten:** EGON STAHL and E. DUMONT, *Talanta*, 1969, **16**, 657. (Institut für Pharmakognosie und Analytische Phytochemie der Universität des Saarlandes, 66 Saarbrücken, B.R.D.)

**Summary**—The possibilities and present applications of gradient thin-layer chromatography are summarized. Methods for the preparation of reproducible and fault-free pH-gradient layers are given. These layers may be characterized by the relationship between pH and position, so that for the first time layers may be produced with a definite gradient profile. Finally, the typical shapes of curves for some classes of compounds after pH-traverse-gradient chromatography are summarized and briefly explained.

ПРИМЕНЕНИЕ ДИГИТАЛЬНЫХ  
ЭЛЕКТРОННЫХ ВЫЧИСЛИТЕЛЕЙ В  
АНАЛИТИЧЕСКОЙ ХИМИИ—I:

C. W. CHILDS, P. S. HALLMAN and D. D. FERRIN, *Talanta*, 1969, 16, 629.

**Резюме**—Дигитальные счетчики применяются в широком диапазоне химических проблем. В статье обсуждаются вопросы которые представляют собой особенный интерес для аналитиков: статистическая обработка результатов, рентгеновский анализ, спектроскопия, масс-спектрометрия, газовая хроматография и электроаналитическая химия.

ОСАЖДЕНИЕ ИЗ ГОМОГЕННЫХ РАСТВОРОВ  
КАТИОНОВ ОСВОБОЖДЕННЫХ ИЗ КОМПЛЕКСОВ  
ЭДТА:

R. GRZESKOWIAK and T. A. TURNER, *Talanta*, 1969, 16, 649.

**Резюме**—Применимость комплексов ЭДТА в осаждении некоторых катионов из гомогенного раствора в разных опытных условиях можно предсказать на основе продукта растворимости осаждаемого соединения и константы устойчивости комплекса. Приведен краткий обзор исследований проведенных до сих пор в области эффективности маскирования. Изучены факторы влияющие на осаждение. Показано что простое отношение позволяет предсказать вероятность осаждения при разных рН и что более тщательные теоретические подходы не нужно дают лучшие результаты.

ОСНОВЫ ГРАДИЕНТОВОЙ ТОНКОСЛОЙНОЙ  
ХРОМАТОГРАФИИ НА «КИСЛОТНОЩЕЛОЧНЫХ»  
СЛОЯХ СИЛИКАГЕЛЯ:

EGON STANL and E. DUMONT, *Talanta*, 1969, 16, 657.

**Резюме**—Обсуждены возможности и современное применение метода градиентовой тонкослойной хроматографии. Приведены методы приготовления воспроизводимых, без дефектов рН-градиентных слоев. Эти слои можно характеризовать на основе отношения между рН и местоположением, так в первый раз приготовлены слои с определенным профилем градиента. В заключение приказаны и объяснены типические кривые некоторых классов соединений, полученные хроматографированием поперечно рН градиента.

**Ion-exchange separation of vanadium, zirconium, titanium, molybdenum, tungsten and niobium:** T. A. FERRARO, *Talanta*, 1969, **16**, 669. (Army Materials and Mechanics Research Center, Watertown, Massachusetts, U.S.A.)

**Summary**—Schemes for the separation of two or more of the elements vanadium, zirconium and/or titanium, molybdenum and tungsten from each other and from relatively large amounts of niobium have been developed, a strongly basic anion-exchange resin being used. Interference from niobium is avoided by using hydrofluoric acid to elute vanadium, zirconium, titanium and molybdenum. The application of coupled columns to improve the efficiency of separation of multi-component mixtures is demonstrated. The use of an "interval" equation defining the volume interval between successively eluted solutes is proposed for calculating the column length required for a particular separation. This equation is especially useful for determining the extent to which a column must be lengthened when overlapping occurs because of high column loading.

**Reaction of gallium and indium with 4-(2-thiazolylazo)resorcinol:** M. LANGOVÁ-HNILIČKOVÁ and L. SOMMER, *Talanta*, 1969, **16**, 681. (Department of Analytical Chemistry, The University, Brno, Czechoslovakia.)

**Summary**—Gallium is shown to react with TAR to form 1:1 and 1:2 Ga:TAR species, elucidation of the nature of which is complicated by hydrolysis. The species  $\text{GaR}^+$  and  $\text{GaHR}(\text{OH})^+$ , where  $\text{H}_2\text{R}$  is the free reagent, occur at pH 2.7–4.8 for solutions that are equimolar or contain excess of metal ion;  $\text{GaHR}^{2+}$  occurs at pH 2.13–2.86 with excess of metal ion. A 1:2 complex, probably  $\text{GaR}_2^-$ , exists in 30% aqueous ethanol medium at pH  $\sim 5$  if excess of ligand is present. The utility of the reaction for analysis is severely limited by the large number of interfering elements. Indium reacts similarly, forming a  $\text{InRH}^{2+}$  complex which is converted into the 1:2 complex by excess of reagent at pH 4.6.

**Bestimmung der freien Säure in Plutonium-, Uran- und Thorium-Lösungen:** HELMUT SCHMIEDER and ERWIN KUHN, *Talanta*, 1969, **16**, 691. (Institut für Heiße Chemie der Gesellschaft für Kernforschung m.b.H., D75 Karlsruhe, B.R.D.)

**Summary**—A method for the determination of free acid in the presence of plutonium, uranium and thorium is described. Since the actinides easily undergo hydrolysis, the titration is performed in a non-aqueous system (2-propanol). Plutonium, uranium and thorium are precipitated as double salts by the addition of caesium chloride. Sodium ethoxide is used as titrant, with phenolphthalein serving as a visual indicator. A photometric titrator has also been tested.

ИОНООБМЕННОЕ РАЗДЕЛЕНИЕ ВАНАДИЯ,  
ЦИРКОНИЯ, ТИТАНА, ВОЛЬФРАМА,  
МОЛИБДЕНА И НИОБИЯ:

Т. А. FERRARO, *Talanta*. 1969, **16**, 669.

**Резюме**—Разработаны схемы разделения двух или выше из элементов ванадия, циркония и/или титана, молибдена и вольфрама одного от другого и от больших количеств ниобия на сильноосновной анионообменной смоле. Влияние ниобия избегнуто использованием фтористоводородной кислоты для элюирования ванадия, циркония, титана и молибдена. Показано применение сопряженных колонок с целью улучшения эффективности разделения многокомпонентных смесей. Предложено «интервальное» уравнение, определяющее объемный интервал между последующими элюированными элементами для расчета длины колонки, необходимой для данного разделения. Это уравнение оказалось особенно полезным для определения удлинения колонки нужного в случае перекрытия пиков в результате перегрузки колонки.

РЕАКЦИЯ ГАЛЛИЯ И ИНДИЯ С  
4-(2-ТИАЗОЛИЛАЗО) РЕЗОРЦИНОМ:

М. LANGOVÁ-HNĚLIČKOVÁ and L. SOMMER, *Talanta*, 1969, **16**, 681.

**Резюме**—Галлий реагирует с ТАР и образует комплексы Ga:ТАР 1:1 и 1:2, разъяснение природы которых осложнено гидролизом.  $\text{GaR}^+$  и  $\text{GaHR}(\text{OH})^+$ , где  $\text{H}_2\text{R}$  представляет собой свободный реагент, существуют при pH 2,7–4,8 в эквимолекулярных растворах или растворах содержащих избыток иона металла;  $\text{GaHR}^{2+}$  существует при pH 2,13–2,86 с избытком иона металла. Комплекс 1:2, вероятно  $\text{GaR}_2^-$ , существует в 30% тном водном растворе этилового спирта при pH ~5 в присутствии избытка лиганда. Применимость реакции в анализе в значительной мере ограничена большим числом мешающих элементов. Индий реагирует подобным образом, образуя комплекс 1:1 который превращается в комплекс 1:2 в присутствии избытка реагента при pH 4,6.

ОПРЕДЕЛЕНИЕ СВОБОДНОЙ КИСЛОТЫ В  
РАСТВОРАХ ПЛУТОНИЯ, УРАНА И ТОРИЯ:

HELMUT SCHMIEDER and ERWIN KUNN, *Talanta*, 1969, **16**, 691.

**Резюме**—Описан метод определения свободной кислоты в присутствии плутония, урана и тория. Поскольку актиниды легко гидролизуют, титрование проводят в неводной системе (2-пропанол). Плутоний, уран и торий осаждаются прибавлением хлорида цезия в форме двойных солей. Этилат натрия служит в качестве титрованного раствора, а фенолфталеин в качестве визуального индикатора. Фотометрический титратор также был испытан.



**Contribution au dosage du glycerol dans les glycerines techniques—II:** R. MORMONT, A. C. GILLET JR. and E. HEINERTH, *Talanta*, 1969, **16**, 701. (Centre de Recherches, Solvay et Cie, S.A., Brussels.)

**Summary**—The authors confirm experimentally the hypothesis of the volatilization of formic acid during the volumetric determination of glycerol by the periodate method. The reproducibility of the results can be improved if sodium formate is added.

**Oxygen determinations with the aluminium corrosion electrode:** E. SCARANO and M. MASCINI, *Talanta*, 1969, **16**, 707. (Institute of Analytical Chemistry, Faculty of Pharmacy, University of Genova, Italy.)

**Summary**—A method for the determination of molecular oxygen in a great variety of liquid and gaseous samples has been developed. The method seems adaptable for control analysis by reason of its sensitivity, rapidity and ease of operation. It gives accurate determinations in the presence of many chemical substances which interfere with other methods. It is based on the variation in corrosion potential of the aluminium electrode, caused by oxygen, and exemplifies use of the corrosion phenomenon in analytical chemistry.

**Analytical aspects of organo-P, As, Sb, S, Se, Te and Sn(IV) (onium) cations:** A. J. BOWD, D. THORBURN BURN; and A. G. FOGG, *Talanta*, 1969, **16**, 719. (Department of Chemistry, Loughborough University of Technology, Loughborough, U.K.)

**Summary**—Reactions and the analytical applications of tetraphenylphosphonium, -arsonium and -stibonium, triphenylmethylarsonium, triphenyl-sulphonium, -selenonium and -telluronium and triphenyltin cations with oxy-anions, and halo- and thiocyanato-anionic complexes are surveyed.

**Coulometrische Metallometrie—Elektrolytisch erzeugter Kupriion als coulometrischer Titrant:** PANTA S. TUTUNĐIĆ and MILAN M. PAUNOVIĆ, *Talanta*, 1969, **16**, 733. (Institut für Physikalische Chemie und Elektrochemie der Technologischen Fakultät der Universität, Belgrad, Jugoslawien.)

**Summary**—Conditions for the quantitative electrolytic dissolution of copper to yield copper(II) ions have been found, and based on this a coulometric titration of anthranilic acid with electrolytically generated copper(II) ions has been developed. The end point is determined amperometrically with two polarized copper electrodes.

**ВКЛАД В ОПРЕДЕЛЕНИЕ ГЛИЦЕРИНА В  
ТЕХНИЧЕСКИХ ГЛИЦЕРИНАХ—II:**

R. MORMONT, A. C. GILLES JR. and E. HEINERTH, *Talanta*, 1969, **16**, 701.

**Резюме**—Авторы подтвердили опытом гипотезу улетучивания муравьиной кислоты при титриметрическом определении глицерина периодатовым методом. Повторяемость результатов улучшали добавлением формиата натрия.

**ОПРЕДЕЛЕНИЕ КИСЛОРОДА С ИСПОЛЬЗОВАНИЕМ  
АЛЮМИНИЕВОГО КОРРОЗИОННОГО ЭЛЕКТРОДА:**

E. SCARANO and M. MASCINI, *Talanta*, 1969, **16**, 707.

**Резюме**—Разработан метод определения молекулярного кислорода в множестве жидких и газообразных веществ. Метод кажется применимым для контрольного анализа на основе его чувствительности, быстроты и легкого использования. Метод позволяет проводить точные определения в присутствии многочисленных химических веществ мешающих другим методам. Метод основан на изменении коррозионного напряжения алюминиевого электрода, вызванного кислородом и служит примером применения коррозии в аналитической химии.

**ПРИМЕНИМОСТЬ В АНАЛИЗЕ ОРГАНИЧЕСКИХ  
КАТИОНОВ P, As, Sb, S, Se, Te И Sn (IV):**

A. J. BOWD, D. THORBURN BURNS and A. G. FOGG, *Talanta*, 1969, **16**, 719.

**Резюме**—Приведен обзор реакций и применений в анализе тетрафенилфосфоний, -арсоний и -стибоний, трифенилметил-арсоний, трифенилсульфоний, -селеноний и -теллуроний и трифенилловокатионов с оксианионами, и галоидными и роданидоанионными комплексами.

**КУЛОНОМЕТРИЧЕСКАЯ МЕТАЛЛОМЕТРИЯ—  
ПРОИЗВЕДЕННЫЙ ЭЛЕКТРОЛИТИЧЕСКИМ ПУТЕМ  
ИОН МЕДИ(II) В КАЧЕСТВЕ  
КУЛОНОМЕТРИЧЕСКОГО ТИТРАНТА:**

PANTA S. TUTUNDŽIĆ and MILAN M. RAUNOVIĆ, *Talanta*, 1969, **16**, 733.

**Резюме**—Исследованы условия для количественного электролитического растворения меди с образованием ионов меди(II) и разработан основывающийся на этих условиях метод кулонометрического титрования антралиновой кислоты с произведенными электролитическим путем ионами меди(II). Конец титрования обнаруживается амперометрическим путем, с использованием двух поляризованных медных электродов.

**Spectrophotometric study of the mercury(II)-Xylenol Orange chelate:** H. H. WALKER and J. A. POOLE, *Talanta*, 1969, **16**, 739. (Department of Chemistry, Temple University, Philadelphia, Pennsylvania, U.S.A.)

**Summary**—The reaction between mercury(II) and Xylenol Orange has been studied in aqueous hexamine medium. The chelate is 1:1 and has an apparent stability constant of  $2.4 (\pm 0.6) \times 10^8$  at pH 7 (2.9*M* hexamine). Beer's law is obeyed over the concentration range 0.5–2.0  $\times 10^{-5}$  *M* mercury(II) when the hexamine concentration is 2.9*M*.

**Rapid spectrophotometric determination of copper in steel with zinc dibenzylthiocarbamate:** OM P. BHARGAVA, *Talanta*, 1969, **16**, 743. (Chemical and Metallurgical Laboratories, The Steel Company of Canada, Limited, Wilcox Street, Hamilton, Ontario, Canada.)

**Summary**—A rapid spectrophotometric method employing zinc dibenzylthiocarbamate is described for determining copper in a wide variety of steels. The acidity is not critical (0.5–2*N*) and the colour of the complex is stable for >1 hr. The range of the method is 0.005–5% copper and 6 samples can be analysed in about an hour.

**Determination of uranium in uraniferous coal:** D. D. PERRICOS and E. P. BELKAS, *Talanta*, 1969, **16**, 745. (Chemistry Division, Nuclear Research Center "Democritos" Athens Greece.)

**Summary**—The uranium content of uraniferous coal has been determined by neutron-activation analysis. Carrier-free  $^{239}\text{Np}$  is separated quantitatively and selectively by column extraction chromatography with glass powder as support and thenoyltrifluoroacetone in xylene as stationary phase. Only one purification step is involved.

ИЗУЧЕНИЕ ХЕЛАТА РТУТИ(II) С  
КСИЛЕНОЛОРАНЖЕВЫМ СПЕКТРОФОТМЕТРИ-  
ЧЕСКИМ МЕТОДОМ:

Н. Н. WALKER and J. A. POOLE, *Talanta*, 1969, **16**, 739.

**Резюме**—Изучена реакция ртути(II) с ксиленолоранжевым в водном растворе гексамина. Хелат 1:1 а его кажущаяся константа устойчивости— $2,4 (\pm 0,6) \times 10^6$  при pH 7 (2,9M раствор гексамина). Закон Бера соблюдается в области концентраций  $0,5-2,0 \times 10^{-5}M$  ртути(II) при концентрации гексамина 2,9M.

БЫСТРОЕ СПЕКТРОФОТОМЕТРИЧЕСКОЕ  
ОПРЕДЕЛЕНИЕ МЕДИ В СТАЛИ С  
ДИБЕНЗИЛДИТИОКАРБАМИНАТОМ ЦИНКА:

Ом. Р. BHARGAVA, *Talanta*, 1969, **16**, 743.

**Резюме**—Описан быстрый спекрофотометрический метод определения меди в разных сталях с использованием дибензилдитиокарбамината цинка. Кислотность не является критической (0,5–2 N), а цвет комплекса устойчивый в течение >1 ч. Диапазон метода 0,005–5% меди. В течение одного часа можно определить 6 образцов.

ОПРЕДЕЛЕНИЕ УРАНА В УРАНОНОСНОМ УГЛЕ:

D. C. FERRICOS and E. P. VELKAS, *Talanta*, 1969, **16**, 745.

**Резюме**—Содержание урана в ураноносном угле определено методом нейтронноактивационного анализа.  $^{239}\text{Np}$  без носителя выделен количественно и селективно с применением метода экстрактивной хроматографии на колонке порошкового стекла, с теноилтрифторэцетоном в ксилоле в качестве стационарной фазы. Нужно провести только однократное очищение.

**Colorimetric determination of zirconium with 1-(2-pyridylazo)-2-naphthol:** L. E. ROSS, V. M. DRABEK and R. P. LARSEN *Talanta*, 1969, **16**, 748. (Argonne National Laboratory, Argonne Illinois, 60439, U.S.A.)

**Summary**—A method is described for the determination of as little as 50 ppm of zirconium in uranium-fission element alloys and zinc-magnesium-uranium-fission element alloys. Zirconium is extracted from a nitric acid-aluminium nitrate medium with dibutyl phosphate in toluene. The uranium co-extracted with the zirconium is removed by scrubbing with hydrochloric acid-ammonium thiocyanate solution. A portion of the organic phase is mixed with pyridine-toluene solution of 1-(2-pyridylazo)-2-naphthol to develop the colour.

**Potentiometric determination of iron with DTPA in the presence of a large amount of aluminium:** RUDOLF PŘIBIL and JAN HORÁČEK, *Talanta*, 1969, **16**, 750. (Laboratory for Analytical Chemistry, J. Heyrovský Polarographic Institute, Czechoslovak Academy of Sciences, Prague 1, Jilská 16, Czechoslovakia.)

**Summary**—Potentiometric determination of iron with DTPA at pH 1.6 (platinum and calomel electrodes) permits determination of iron in the presence of aluminium up to an Al:Fe ratio of 70. Aluminium is determined indirectly by addition of excess of DCTA, adjustment to pH 5, and back-titration with iron(III) chloride.

**Separation and solvent extraction of vanadium and uranium with n-propyl 2,3,4-trihydroxybenzoate:** FADIL JASIM, *Talanta*, 1969, **16**, 752. (Department of Chemistry and Food Technology, College of Agriculture, University of Baghdad, Baghdad, Iraq.)

**Summary**—A spectrophotometric method is described for the separation and determination of trace quantities of vanadium(IV) and (V) from uranium(VI). Vanadium is selectively separated from uranium by extraction at pH 6.5 into n-propyl 2,3,4-trihydroxybenzoate (PTB) dissolved in t-pentanol. Up to 120  $\mu\text{g}$  of vanadium can be determined by measuring the absorbance of the blue complex in the organic phase at 585 nm. Uranium(VI) remains in the aqueous layer and can be determined spectrophotometrically by its reaction with PTB in aqueous acetone to produce a brown-red colour at pH 7.6–8.8. Solutions containing 25–275  $\mu\text{g}$  of uranium absorb at 370–380 nm according to Beer's law. By modification, this procedure can be used for the determination of the two metals in native phosphate rocks. The effects of diverse ions on the determination of vanadium and uranium have also been examined.

### КОЛОРИМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ЦИРКОНИЯ 1-(2-ПИРИДИЛАЗО)-2-НАФТОЛОМ:

L. E. ROSS, V. M. DRABEK and R. P. LARSEN, *Talanta* 1969; **16**, 748.

**Резюме**—Описан метод определения только 50 мкг/г циркония в сплавах элементов расщепления урана и сплавах цинка, магния и элементов расщепления урана. Цирконий извлекают из раствора азотной кислоты и нитрата алюминия раствором дибутилфосфата в толуоле. Извлеченный одновременно с цирконием уран удаляют промывкой раствором соляной кислоты и роданида аммония. Часть органической фазы смешивают с раствором 1-(2-пиридилазо)-2-нафтола в пиридине и толуоле для проявления окраски.

### ПОТЕНЦИОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ЖЕЛЕЗА С ДЦТА В ПРИСУТСТВИИ БОЛЬШЕЙ КОНЦЕНТРАЦИИ АЛЮМИНИЯ:

RUDOLF PŘIBIL and JAN HORÁČEK, *Talanta*, 1969, **16**, 750.

**Резюме**—Потенциометрическое определение железа с ДЦТА при рН 1,6 (платиновый и каломелевый электроды) позволяет определять железо в присутствии алюминия все до отношения Al:Fe 70:1. Алюминий определяют косвенным методом—добавлением избытка ДЦТА, приведением рН до 5 и оттитровыванием с раствором железо(III)хлорида.

### РАЗДЕЛЕНИЕ И ЭКСТРАКЦИЯ ВАНАДИЯ И УРАНА Н-ПРОПИЛ-2,3,4-ТРИОКСИБЕНЗОАТОМ:

FADIL JASIM, *Talanta*, 1969, **16**, 752.

**Резюме**—Описан спектрофотометрический метод разделения и определения следовых количеств ванадия(IV) и (V) от урана(VI). Ванадий селективно отделяют от урана извлечением при рН 6,5 раствором н-пропил-2,3,4-триоксibenзоата (ПТБ) в т-пентаноле. Метод позволяет определить до 120 мкг ванадия измерением светопоглощения голубого комплекса в органической фазе при 585 нм. Уран(VI) остается в водном слое и его можно определить спектрофотометрическим методом основанным на его реакции с ПТБ в водном растворе ацетона с образованием коричневокрасной окраски при рН 7,6–8,8. Содержащие 25–275 мкг урана растворы поглощают при 370–380 нм с соблюдением закона Бера. Несколько измененный метод позволяет определять эти два металла в фосфатных горных породах. Изучено влияние разных ионов на определение ванадия и урана.

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## Contents

### Talanta Medal

C.W.CHILDS, P.S.HALLMAN and D.D.PERRIN: **Talanta Review:** Applications of digital computers analytical chemistry—I

R.GRZESKOWIAK and T.A.TURNER: Precipitation from homogeneous solution of cations released from EDTA complexes

E.STAHL and E.DUMONT: Grundlagen der Gradient-Dünnschicht-Chromatographie auf "Säure-Basischen" Kieselgel-Schichten

T.A.FERRARO: Ion-exchange separation of vanadium, zirconium, titanium, molybdenum, tungsten and niobium

M.LANGOVÁ-HNILÍKOVÁ and L.SOMMER: Reaction of gallium and indium with 4-(2-thiazolyl)arsorcinol

H.SCHMIEDER and E.KUHN: Bestimmung der Freien Säure in Plutonium-, Uran- und Thorium-Lösungen

R.MORMONT, A.C.GILLET, JR. et E.HEINERTH: Contribution au dosage du glycérol dans les glycérol techniques—II

E.SCARANO and M.MASCINI: Oxygen determinations with the aluminium corrosion electrode

A.J.BOWD, D.THORBURN BURNS and A.G.FOGG: Analytical aspects of organo-P, As, Sb, S, Se, and Sn(IV) (onium) cations

P.S.TUTUNĐIĆ and M.M.PAUNOVIĆ: Coulometrische Metallometrie. Elektrolytisch erzeugte Kupriion als coulometrischer Titrant

### Short Communications

H.H.WALKER and J.A.POOLE: Spectrophotometric study of the mercury (II)-Xylenol Orange chelate

O.M.P.BHARGAVA: Rapid spectrophotometric determination of copper in steel with zinc dibenzylidithiocarbamate

D.C.PERRICOS and E.P.BELKAS: Determination of uranium in uraniumiferous coal

L.E.ROSS, V.M.DRABEK and R.P.LARSEN: Colorimetric determination of zirconium with 1-pyridylazo-2-naphthol

R.PŘIBIL and J.HORÁČEK: Potentiometric determination of iron with DTPA in the presence of a large amount of aluminium

FADIL JASIM: Separation and solvent extraction of vanadium and uranium with n-propyl 2,3,4-trihydroxybenzoate

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