

techniques (21) for chopping a laser beam at megahertz frequencies and high frequency lock-in amplification both exist, suggesting the practicability of a more quantitative dispersive PAS of solids. The corresponding high frequency FTPAS experiment probably can be performed using the train of nanosecond duration white light pulses from a synchrotron as the intense high frequency light source. Such an exotic FTPAS experiment offers little prospect of an advantage over megahertz dispersive PAS at visible wavelengths unless speed of acquisition of a broad band spectrum assumes paramount importance.

ACKNOWLEDGMENT

We have had numerous interesting discussions with Joel M. Harris, University of Utah, and also thank William A. Koldewyn, IBM-Boulder, for suggestions regarding the He-Ne laser interferometric referencing system.

LITERATURE CITED

- (1) A. G. Bell, *Am. J. Sci.*, **20**, 305 (1880).
- (2) A. G. Bell, *Phil. Mag.*, **11**, 510 (1881).
- (3) A. Rosencwaig, *Opt. Commun.*, **7**, 305 (1973).
- (4) A. Rosencwaig, *Anal. Chem.*, **47**, 592 (1975).
- (5) A. Rosencwaig and A. Gersho, *J. Appl. Phys.*, **47**, 64 (1976).
- (6) A. Rosencwaig, *Adv. Electron. Electron Phys.*, **46**, 207 (1978).
- (7) D. Cahen and H. Garty, *Anal. Chem.*, **51**, 1865 (1979).
- (8) J. W.-P. Lin and L. P. Dudek, *Anal. Chem.*, **51**, 1627 (1979).

- (9) C. K. N. Patel, A. C. Tam, and R. J. Kerl, *Appl. Phys. Lett.*, **34**, 467 (1979).
- (10) A. Hordvik and H. Schlossberg, *Appl. Opt.*, **11**, 101 (1977).
- (11) M. M. Farrow, R. K. Burnham, M. Auzanneau, S. L. Olsen, N. Purdie, and E. M. Eyring, *Appl. Opt.*, **17**, 1093 (1978).
- (12) H. K. Wickramasinghe, R. C. Bray, V. Jipson, C. F. Quater, and J. R. Salcedo, *Appl. Phys. Lett.*, **33**, 923 (1978).
- (13) M. M. Farrow, R. K. Burnham, and E. M. Eyring, *Appl. Phys. Lett.*, **33**, 735 (1978).
- (14) G. Busse and B. Bullemer, *Infrared Phys.*, **18**, 255 (1978).
- (15) M. G. Rockley, *Chem. Phys. Lett.*, **68**, 455 (1979).
- (16) P. R. Griffiths, "Chemical Infrared Fourier Transform Spectroscopy", John Wiley and Sons, New York, 1975, p 40.
- (17) C. Foskett and T. Hirschfeld, *Appl. Spectrosc.*, **31**, 239 (1977).
- (18) Representative examples are: W. N. Deigass, G. L. Haller, R. Kellerman, and J. H. Lunsford, "Spectroscopy in Heterogeneous Catalysis", Academic Press, New York, 1979, Chapter 4. R. Tilgner and E. Lushcer, *Z. Phys. Chem. N.F.*, **111**, 19 (1978).
- (19) M. J. Adams, B. C. Beadle, A. A. King, and G. F. Kirkbright, *Analyst (London)*, **101**, 553 (1976).
- (20) J. J. Freeman, R. M. Friedman, and H. C. Reichard, *J. Phys. Chem.*, **84**, 315 (1980).
- (21) J. Sapriel, "Acousto-Optics", John Wiley and Sons, New York, 1979, Chapter 7.

RECEIVED for review December 26, 1979. Accepted June 20, 1980. The blood studies performed by LBL and WLC were made possible by Grant HL 23378-01 from the National Heart, Lung, and Blood Institute. The applications of FTPAS to the study of solid samples were financed by a contract from the Department of Energy (Office of Basic Energy Sciences).

Dissociation Constants of Acetic Acid and Primary Phosphate Ion and Standards for pH in 10, 20, and 40 wt % Ethanol/Water Solvents at 25, 0, -5, and -10 °C

Roger G. Bates,* H. P. Bennetto,¹ and Munessar Sankar²

Department of Chemistry, University of Florida, Gainesville, Florida 32611

Earlier work leading to the standard potential of the Ag/AgCl electrode in 10, 20, and 40 wt % ethanol/water solvents at 25, 0, -5, and -10 °C has been extended to the study of an acetate buffer solution and a phosphate buffer solution in the same media at these four temperatures. Cells without liquid junction,



were used to determine the dissociation constants of acetic acid and H₂PO₄⁻ in these ethanol/water media. Buffer solutions composed of (a) acetic acid (0.05 m), sodium acetate (0.05 m) and (b) KH₂PO₄ (0.025 m), Na₂HPO₄ (0.025 m), where m is molality, are useful as standards for pH measurements.

In a recent contribution (1), we have reported a determination of the standard potential of the silver-silver chloride electrode in 10, 20, and 40 wt % ethanol/water solvents at four temperatures: 25, 0, -5, and -10 °C. The results lay the groundwork for thermodynamic studies, by emf methods, of both weak and strong electrolytes in these solvent media at temperatures below 0 °C. We have now investigated the

dissociation of two weak acids of different charge types, namely, acetic acid and H₂PO₄⁻, and have determined conventional pH values for an acetate buffer solution and a phosphate buffer solution in ethanol/water media at subzero temperatures. These solutions are useful as reference standards for pH measurements and control in such processes as the separation of the protein fractions of blood plasma by the Cohn method (2).

EXPERIMENTAL

Glacial acetic acid was purified by repeated fractional freezing under nitrogen. The melting point of the product rose in five stages of purification from 14.5 to 16.602 °C; this final value is to be compared with the literature value of 16.606 °C. Sodium acetate and sodium chloride were crystallized twice from doubly distilled water. The former was dried at 120 °C overnight and finally for 3 h under vacuum at 95 °C. The NaCl was dried at 130-150 °C in air. The KH₂PO₄ and Na₂HPO₄ were NBS Standard Reference Materials 1861c and 1861I; they were dried for 2 h under vacuum at 100 °C.

Stock solutions containing equal molal ratios, HAc/NaAc and KH₂PO₄/Na₂HPO₄, in the appropriate mixture of water and absolute ethanol were prepared. The cell solutions were prepared by weight from these stock solutions, the ethanol/water solvents, and NaCl. Limited solubility in 40 wt % ethanol precluded the measurements of phosphate-NaCl solutions in this solvent at 0 °C and below. Likewise, some problems were encountered with freezing of the acetate buffers in 10 wt % ethanol at -10 °C. One of the phosphate buffer solutions in 10% ethanol also froze after some time at -10 °C, but no difficulty was experienced in obtaining

¹ On leave from Queen Elizabeth College, University of London, 1979.

² On leave from the University of Durban-Westville, South Africa, 1977-78.

Table I. Electromotive Force of Cells A and B for Three Ethanol/Water Solvents at 25, 0, -5, and -10 °C, in Volts

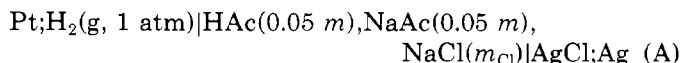
<i>t</i> , °C	<i>m</i> _{Cl} , mol kg ⁻¹	10% EtOH	20% EtOH	40% EtOH
Cell A (0.05 <i>m</i> HAc + 0.05 <i>m</i> NaAc)				
25	0.03	0.59547	0.59773	0.61138
	0.02	0.60592	0.60818	0.62194
	0.01	0.62375	0.62600	0.63983
0	0.03	0.57736	0.57802	0.59412
	0.02	0.58690	0.58757	0.60372
	0.01	0.60321	0.60394	0.62012
-5	0.03	0.57358	0.57378	0.59052
	0.02	0.58290	0.58320	0.60001
	0.01	0.59891	0.59913	0.61606
-10	0.03	(solutions froze)	0.56948	0.58691
	0.02		0.57864	0.59626
	0.01		0.59429	0.61190
Cell B (0.025 <i>m</i> KH ₂ PO ₄ + 0.025 <i>m</i> Na ₂ HPO ₄)				
25	0.03	0.72977	0.73518	0.73934
	0.02	0.74099	0.74653	0.75125
	0.01	0.75954	0.76535	0.77075
0	0.03	0.70676	0.71160	(salts incompletely soluble)
	0.02	0.71705	0.72207	
	0.01	0.73409	0.73938	
-5	0.03	0.70211	0.70670	
	0.02	0.71224	0.71702	
	0.01	0.72902	0.73403	
-10	0.03	0.69751	0.70169	
	0.02	0.70747	0.71184	
	0.01	0.72396	0.72858	

equilibrium values of the emf before freezing occurred. Nevertheless, it is unlikely that this buffer solution will prove useful for pH control at -10 °C.

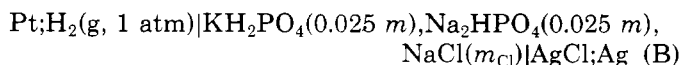
The preparation of electrodes and other experimental details were the same as in the earlier work (1). Again the cells displayed excellent stability; final emf values at 25 °C, obtained after the measurements at 0, -5, and -10 °C were concluded, usually agreed with the initial values within 0.06 mV. In most instances, cells were measured in duplicate, the two measurements agreeing, on the average, to about 0.05 mV.

RESULTS AND DISCUSSION

The cells used for the measurements can be represented by



and



where Ac is acetate and *m* is molality (moles per kilogram of mixed solvent). The observed data, corrected to a partial pressure of hydrogen of 1 atm (101.325 kPa) as described earlier (1), are listed in Table I.

The relationship between the emf (*E*), the standard emf of the cell (*E*⁰), and the thermodynamic *pK* value for each of the acids was formulated as follows:

$$pK' \equiv pK - \beta I = \frac{(E - E^0)F}{2.3026RT} + \log m_{\text{Cl}} + \log \frac{m_{\text{acid}}}{m_{\text{base}}} + \frac{nAI^{1/2}}{1 + 4.57BI^{1/2}} \quad (1)$$

where *I* is the ionic strength, *A* and *B* are constants of the Debye-Hückel theory (1), and *n* is a coefficient dependent on the charge type of the acid-base pair. The *pK* was determined by linear regression methods from the values of *pK'* for each solution studied. For the acetate system, *n* = 0. The

buffer ratio *m*_{acid}/*m*_{base}, that is, *m*_{HAc}/*m*_{Ac}, was obtained by correcting the stoichiometric molalities (0.05) for the dissociation of acetic acid. In order to make this small correction, concentrations of hydrogen ion were derived from the *p**a*_H obtained as described below. For the phosphate system, *n* = 2; hydrolysis of the phosphate ions was so slight that *m*_{acid}/*m*_{base} did not depart significantly from unity.

The conventional activity *pH* (-log *a*_H) values for the chloride-free acetate and phosphate buffers were calculated from the limiting value, *p*(*a*_Hγ_{Cl})⁰, of the acidity function *p*(*a*_Hγ_{Cl})

$$p(a_{\text{H}}\gamma_{\text{Cl}}) = \frac{(E - E^0)F}{2.3025RT} + \log m_{\text{Cl}} \quad (2)$$

at *m*_{Cl} = 0:

$$p a_{\text{H}} = p(a_{\text{H}}\gamma_{\text{Cl}})^0 + \log \gamma_{\text{Cl}} \quad (3)$$

The convention

$$-\log \gamma_{\text{Cl}} = \frac{AI^{1/2}}{1 + B\hat{a}I^{1/2}} \quad (4)$$

was utilized, with \hat{a} , the ion-size parameter, = 4.57 Å; this is the same as its conventional value (1.5/*B*) in aqueous solutions (3). This value, which was chosen earlier to derive *p**a*_H in methanol-water solvents (4), was also used to calculate *pK'* by Equation 1. Hydrolysis of the acidic and basic species makes a negligible contribution to the ionic strength of these solutions. Hence, for acetate buffers

$$I = 0.05 + m_{\text{Cl}} \quad (5)$$

and for the phosphate buffers

$$I = 0.1 + m_{\text{Cl}} \quad (6)$$

The standard potential *E*⁰ (molality scale) of the cell was reported in our earlier paper (1). Apparent values (*E*⁰) were a function of the ionic strength and the choice of ion-size parameter \hat{a} . The criterion of a minimum in the standard deviation for regression from the linear plot of *E*⁰ as a function of *I* was adopted. This procedure yielded reasonable values of \hat{a} of 4.8 to 6.3 Å in 10% ethanol and 4.0 to 5.2 Å in 40% ethanol. At the intermediate composition (20% ethanol), however, \hat{a} appeared to range from 6.2 to 8.5 Å at the four temperatures, 25 to -10 °C, despite a high degree of precision in the measurements.

This anomaly has prompted us to re-examine the calculation of *E*⁰, and for this purpose we have now applied the activity coefficient equation of Bennetto and Spitzer (5), based on a polarizable spheres model. The results of this treatment are in good agreement with the earlier calculations at 10 and 40% ethanol but yield lower values of \hat{a} and *E*⁰ for the 20% ethanol solvent. The mean difference of about 0.3 mV corresponds to 0.005 in *pH*. The values of \hat{a} found by this procedure vary linearly with the temperature, but there is a suggestion that \hat{a} , at a given temperature, passes through a minimum at a solvent composition between 10 and 20 wt % ethanol.

The results of this calculation are compared with the previous results in Table II. The mean values of *E*⁰, given in the last column, were used to derive *pK'* and *p*(*a*_Hγ_{Cl}) by Equations 1 and 2, respectively. The values of *p*(*a*_Hγ_{Cl})⁰ at *m*_{Cl} = 0 were determined by linear regression of *p*(*a*_Hγ_{Cl}) as a function of *m*_{Cl}, whereas *pK* at *I* = 0 was found by linear regression of *pK'* vs. *I*. The results for *pK* and *p**a*_H are summarized in Table III. These quantities are self-consistent, that is, they are interrelated through the identity

$$pK = p a_{\text{H}} + \frac{(n + 1)AI^{1/2}}{1 + 4.57BI^{1/2}} + \beta I \quad (7)$$

derived from the mass law. As indicated above, *n* = 0 for

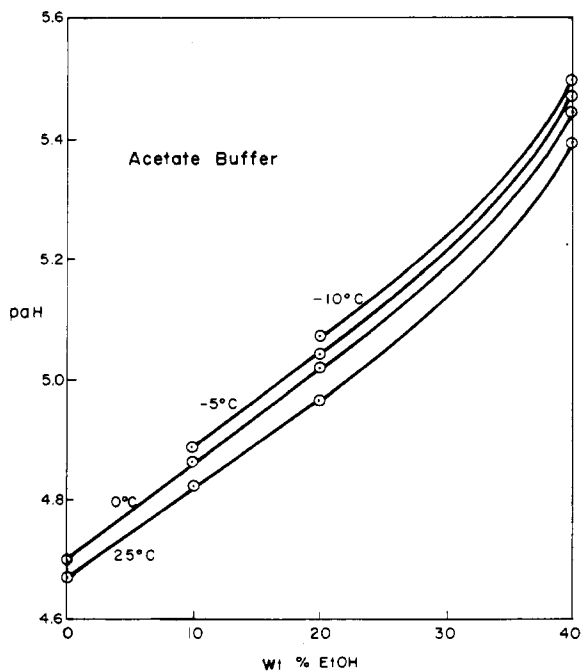


Figure 1. $p\text{a}_\text{H}$ of the acetate buffer solution at four temperatures as a function of the composition of the ethanol/water solvent

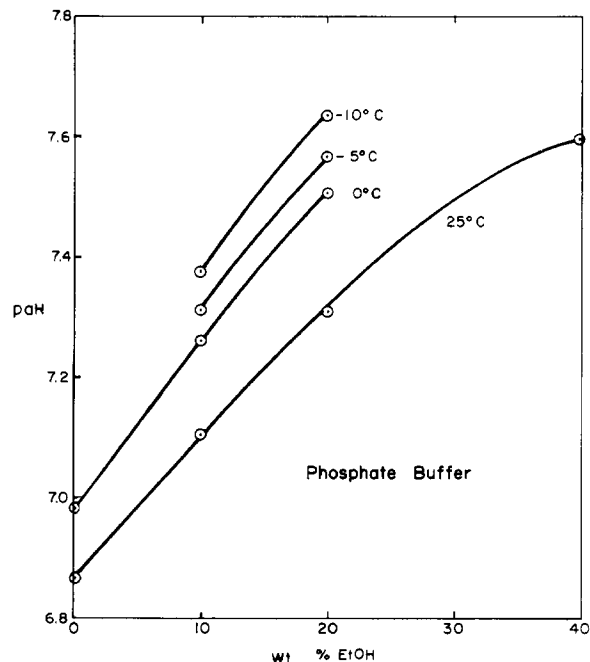


Figure 2. $p\text{a}_\text{H}$ of the phosphate buffer solution at four temperatures as a function of the composition of the ethanol/water solvent

Table II. Standard Emf (E°) of the Cell at Four Temperatures

t , $^\circ\text{C}$	Previous results (1)		Recalculated results		mean E° , V
	a , A	E° , V	a , A	E° , V	
10% ethanol					
25	4.8	0.21458	5.6	0.21455	0.21457
0	5.8	0.22619	6.15	0.22614	0.22617
-5	6.2	0.22773	6.2	0.22763	0.22768
-10	6.3	0.22886	6.35	0.22878	0.22881
20% ethanol					
25	6.2	0.20771	5.5	0.20750	0.20761
0	8.0	0.21781	6.1	0.21750	0.21766
-5	8.5	0.21883	6.2	0.21849	0.21866
-10	8.2	0.21941	6.25	0.21910	0.21926
40% ethanol					
25	4.0	0.19450	4.8	0.19446	0.19448
0	4.5	0.20972	5.2	0.20970	0.20971
-5	4.8	0.21197	5.25	0.21183	0.21190
-10	5.2	0.21395	5.3	0.21385	0.21390

acetic acid and $n = 2$ for H_2PO_4^- . The changes of $p\text{a}_\text{H}$ for the two buffer solutions with temperature and solvent composition are shown in Figures 1 and 2.

Spivey and Shedlovsky (9) have determined the dissociation constant of acetic acid in ethanol/water mixtures by means of measurements of electrolytic conductance over a range of solvent compositions at 0, 25, and 35 $^\circ\text{C}$. Our results in 10, 20, and 40 wt % ethanol can be compared with theirs at 25 and 0 $^\circ\text{C}$. For this purpose, we have corrected their values on the molar concentration scale (pK_c) to values on the molality scale (pK_m) by use of the solvent density, d_0 :

$$pK_m = pK_c + \log d_0 \quad (8)$$

The agreement between the two determinations is excellent in 10 and 40 wt % ethanol; the differences amount to 0.004 and 0.007 at 25 and 0 $^\circ\text{C}$, respectively, in 10% ethanol and to 0.003 and 0.006, respectively, in 40% ethanol. A larger discrepancy (0.017 unit) appears in 20% ethanol at 25 $^\circ\text{C}$, and a still larger difference of 0.050 unit is found at 0 $^\circ\text{C}$. A plot of pK_m as a function of wt % ethanol (Figure 3) makes it clear that this latter result is inconsistent both with their other data and with ours and may be presumed to be in error.

As far as we are aware, there have been no previous attempts to provide reference solutions for the standardization

Table III. pK of Acetic Acid and H_2PO_4^- in Four Ethanol/Water Solvents. Conventional $p\text{a}_\text{H}$ Values for an Acetate and a Phosphate Buffer

t , $^\circ\text{C}$	H_2O		10% EtOH		20% EtOH		40% EtOH	
	pK^a	$p\text{a}_\text{H}$	pK	$p\text{a}_\text{H}$	pK	$p\text{a}_\text{H}$	pK	$p\text{a}_\text{H}$
0.05 m HAc + 0.05 m NaAc								
25	4.756	4.670	4.919	4.822	5.075	4.967	5.539	5.395
0	4.770	4.687	4.956	4.861	5.131	5.021	5.580	5.445
-5	-	-	4.974	4.881	5.149	5.044	5.605	5.470
-10	-	-	-	-	5.177	5.075	5.628	5.498
0.025 m KH_2PO_4 + 0.025 m Na_2HPO_4								
25	7.198	6.865	7.529	7.104	7.800	7.310	8.287	7.597
0	7.313	6.984	7.695	7.263	8.017	7.508	-	-
-5	-	-	7.758	7.315	8.083	7.569	-	-
-10	-	-	7.825	7.376	8.157	7.638	-	-

^a In H_2O : pK of acetic acid from Ref. 6 and 7; pK of H_2PO_4^- from Ref. 8.

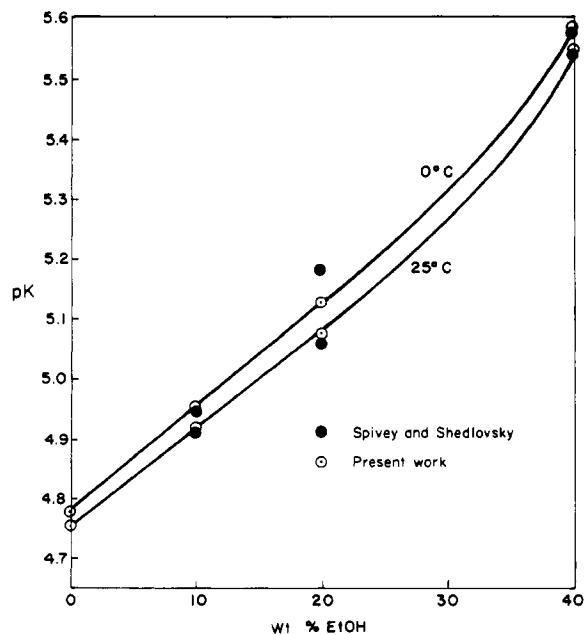


Figure 3. pK (molality scale) for acetic acid in ethanol/water mixtures at 0 and 25 °C as a function of the composition of the solvent. Data in water are from Ref. 6 and 7

of pH measurements in ethanol/water media at temperatures below 0 °C. The values of $p\alpha_H$ for the acetate and phosphate buffers given in Table III may fill this need. When used as reference solutions, the $p\alpha_H$ of these buffer solutions is

identified with pH(S) in the operational definition of pH. Nevertheless, too little is yet known concerning the residual liquid-junction potential in these solvents at low temperatures to permit one to assess the internal consistency of the pH scale defined by these reference points. Measurements of pH under these extreme conditions are rendered difficult by the extraordinarily high resistance of the usual glass electrodes. In addition, modified reference electrodes will doubtless prove a necessity.

LITERATURE CITED

- (1) M. Sankar, J. B. Macaskill, and R. G. Bates, *J. Solution Chem.*, **8**, 887 (1979).
- (2) E. J. Cohn, F. R. N. Gurd, D. M. Surgenor, B. A. Barnes, R. K. Brown, G. Deronau, J. M. Gillespie, F. W. Kahnt, W. F. Lever, C. H. Liu, D. Mittelman, R. F. Mouton, K. Schmid, and E. Uroma, *J. Am. Chem. Soc.*, **72**, 465 (1950).
- (3) R. G. Bates and E. A. Guggenheim, *Pure Appl. Chem.*, **1**, 163 (1960).
- (4) M. Paabo, R. A. Robinson, and R. G. Bates, *J. Am. Chem. Soc.*, **87**, 415 (1965).
- (5) H. P. Bennetto and J. J. Spitzer, *J. Chem. Soc., Faraday Trans. 1*, **73**, 1066 (1977).
- (6) H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.*, **54**, 1350 (1932); **55**, 652 (1933).
- (7) D. A. MacInnes and T. Shedlovsky, *J. Am. Chem. Soc.*, **54**, 1429 (1932).
- (8) R. G. Bates and S. F. Acree, *J. Res. Natl. Bur. Stand.*, **34**, 373 (1945).
- (9) H. O. Spivey and T. Shedlovsky, *J. Phys. Chem.*, **71**, 2171 (1967).

RECEIVED for review March 3, 1980. Accepted May 12, 1980. This work was supported in part by the National Science Foundation under Grant CHE76 24556. M.S. thanks the following organizations in the Republic of South Africa for financial assistance: the C.S.I.R., Ernest Oppenheimer Memorial Trust, and Sentrachem Ltd.

Determination of Oxidation States of Uranium in Uranium Dioxide Pellets by Two-Step Flow-Coulometry

Sorin Kihara,* Zenko Yoshida, Hiroshi Muto, Hisao Aoyagi, Yuji Baba, and Hiroshi Hashitani*

Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki-ken, Japan

A chemical method for analysis of distribution of oxidation states of metals in solids has been developed as a reference to other methods based on physical measurements. A solid is dissolved with a continuous flow of strong phosphoric acid from surface to bulk, and oxidation states of the dissolved ions are determined consecutively by two-step flow-coulometry. Strong phosphoric acid dissolves such solids as uranium or iron oxides to ions whose oxidation states are the same as those in solids. The oxidized surface of about 20 Å on a UO₂ pellet which had stood for about 10 years at room temperature in air was estimated to be UO_{2.05}, and the O/U ratio decreased toward the bulk until 0.1 μm. After the pellet was heated for 10 h at 300 or 430 °C in air, the oxidized surface layer increased to about 8 μm (400 Å of powdered U₃O₈ + UO_{2+x}, 0.66 > x > 0.01) or about 820 μm (370 μm of powdered U₃O₈ + 3 μm of U₃O₈ + 450 μm of UO_{2+x}, 0.66 > x > 0.01), respectively.

Analysis of oxidation states of metals in solids based on physical measurements gives abundant information on ma-

terial science. These physical methods can be classified broadly into methods (1) for analysis of very thin layers at the surface such as by X-ray photoemission spectrometry (XPS) or Auger electron spectrometry (AES) and methods (2) which give overall information on a solid such as measurements of conductivity or electromotive force (EMF). There are many difficulties still remaining with these methods. In the former, for example, pretreatment of the surface and composition of the matrix greatly affect the result of analysis, and, in the latter, interaction between sample and electrode and the presence of impurities often give serious trouble. Therefore, calibration by reference materials and careful evaluation of data obtained are required. Obviously, data obtained by chemical analyses offer many suggestions for the interpretation of results obtained by physical methods.

Although analyses of oxidation states by chemical methods give rather quantitative results, most of the work using these methods has been done to obtain the overall oxidation state of a sample. Few attempts have been made to analyze oxidized films of solid surfaces or to determine distribution of oxidation states in a solid.

The objective of our research was to develop a new independent method to investigate the distribution of oxidation