

served for dopamine, catechol, and *p*-hydroquinone is consistent with the influence of a hydrogen-atom transfer pathway, although these reactions are complicated by adsorption (8, 30).

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Evaluation of Geochemical Standard Reference Materials for Microanalysis

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National Bureau of Standards Coal Fly Ash SRM 1633a gave relative standard deviations $\leq 20\%$ for replicate determinations of 24 elements using sample aliquots of less than 5.45 mg. Sample heterogeneity was noted for Ba, Se, and Ni. U.S. Geological Survey standard rock BCR-1 was found to be homogeneous at sample weights less than 7.011 mg, although poorer than expected precision was observed for Ni, Cr, Dy, and Ho. A standard pottery, SP, was homogeneous for all elements measured using sample weights less than 1.034 mg. The three standards are sufficiently homogeneous for use in microanalysis, except for the elements noted.

In trace-element methods such as proton-induced X-ray emission (PIXE), laser-microprobe mass analysis (LAMMA),

solid sample graphite furnace atomic absorption (GFAA), and solid sample inductively coupled plasma (ICP) emission spectroscopy, sample mass is limited by instrumental constraints (e.g., target thickness, atomization volume, etc.) to milligram or submilligram amounts. Instrumental neutron activation analysis (INAA), prompt γ activation analysis (PGAA), conventional X-ray fluorescence (XRF), and several other methods have no inherent constraints, but sample size may be limited by practical considerations (e.g., induced radiation level for high neutron fluences). In the analysis of air particulates, single mineral grains, or meteorite microinclusions, sample availability dictates very small sample sizes.

The problems of both standardization and quality control (QC) in methods requiring milligram or submilligram sample sizes are more serious than those found in macroanalysis (1-3) because of the lack of certified standards for microanalysis.

Methods which suffer from matrix effects, e.g., XRF, PIXE, and GFAA require standards similar in composition to unknowns and QC programs should ideally include certified or well-calibrated natural materials. Recently Gries (4) prepared multielement standards for GFAA, XRF, LAMMA, and SSMS by ion implantation. Ion exchange beads (5) and thin-film gelatin standards (6) have been proposed for LAMMA and SIMS and Headridge and Riddington (7) discussed the use of metal powder standards for solid sample GFAA of alloys.

The National Bureau of Standards' certified Standard Reference Materials (SRMs) have proved valuable as trace element standards and as secondary standards in QC for the analysis of environmental, geological, biological, and energy related materials, and noncertified geochemical standards issued by the U.S. Geological Survey (8) have been used extensively. Although relatively few elements are certified for NBS Standards, large data bases have accumulated on certified and noncertified elements in NBS Standards (9) and in USGS Standards (8, 10) which make these materials particularly valuable to the analyst.

Geochemical and environmental standards are heterogeneous; they contain different mineralogical species and a range of particle sizes. Sampling gives rise to a statistical sampling error, the magnitude of which depends on the weight of sample, the number of components, grain size distribution, the densities of the particles, and the distribution of the analyte among the components. Several authors (11–13) have expressed the sampling error $S(\%)$ for binary and pseudobinary mixtures; thus Wilson (11) derived the equation

$$S(\%) = 100 \frac{C_A - C_B}{C} \left[f_A f_B \frac{d_A d_B}{d} \frac{4\pi \bar{r}^3}{3W} \right]^{1/2} \quad (1)$$

where C_A and C_B are the concentrations of element in components A and B, C is the concentration of element in sample, d_A and d_B are the densities of components A and B (g cm^{-3}), d is the sample density (g cm^{-3}), \bar{r} is the mean radius of particles (cm), W is the weight of sample (g), and f_A and f_B are the weight fractions of components A and B.

The sampling error, $S(\%)$, may be the largest contribution to overall error in microanalytical methods and, in practice, it is minimized by decreasing particle size (grinding) or by increasing sampling weight. Thus for NBS SRMs, the maximum particle size (mesh through which entire sample is sieved) is quoted and minimum sample sizes are specified for which the material is homogeneous for the elements certified. Sample weights are generally 100–250 mg for environmental, geochemical, and fossil fuel standards (e.g., coals SRM 1632, 1632a, 1635; fly ashes SRM 1633, 1633a; and air particulates SRM 1648). Trace element standards for microanalysis must have small sampling error at the milligram or submilligram size and thus should be of small particle size, homogeneous mineralogical content, and uniform distribution of minor elements among components. Of the NBS geochemical SRMs, these conditions may be met by fine-grained volcanic rocks, e.g., basalt (SRM 688), and obsidian (SRM 278), or coal fly ashes (SRM 1633 and 1633a). Fly ashes are particularly suitable natural matrices because of the high content of very fine spherical particles ($<50 \mu\text{m}$ diameter) of relatively homogeneous, predominantly glass, composition, a result of mineral melting during coal combustion. Recently Ng et al. (14) measured reproducibility for six elements in SRM 1633a using solid-injection (0.5–2.5 mg) ICP and reported $<12\%$ relative standard deviation. Korotev and Lindstrom (15) showed that $<10\%$ RSD should be associated with many trace elements determined by INAA in 10-mg aliquots of SRM 1633a. The USGS basalt BCR-1 standard rock and the standard pottery (SP) prepared from a doped and fired clay

Table I. Elemental Standards Used for INAA of NBS SRM 1633, 1633a, and 1632

elements determined	standard used
Ti, V, Cl, Se, Sm, Br, Ga, Na, Mn	NBS Coal SRM 1632
Al, Mg, Ba, Sr, Sc, U, Ca, Cs	NBS Fly Ash 1633
As, Rb, Sb, Zn Hf, Zr, Ce, Eu, Ta, Tb, Th	NBS Orchard Leaves SRM 1571 U.S.G.S. GSP-1
Fe, Ni, Co, Cr	U.S.G.S. Dunite DTS-1

matrix by Perlman and Asaro (16), which has been characterized for 13 trace elements, are also potential standards.

This paper evaluates the homogeneity of NBS SRM 1633a, USGS BCR-1, and SP as trace element standards for sample sizes ranging from 100 to 7000 μg . Comparison data for NBS 1633 and 1632, bituminous coal, using larger sample weights, are also presented. The three standards are suitable for use at submilligram and milligram weights for most elements investigated except for Ni, Se, Ba, and Tb in SRM 1633a, and for Cr, Ni, Dy, and Ho in BCR-1. Although BCR-1 and SP are no longer available, many laboratories still use these standards.

EXPERIMENTAL SECTION

Samples of NBS Bituminous Coal SRM 1632 (30.1–30.2 mg) and NBS Coal Fly Ash 1633 (19.3–20.3 mg) were weighed into HNO_3 -cleaned 1-mL irradiation vials which were heat sealed. The small mass samples (0.95–5.45 mg) of NBS 1633a were prepared by weighing the fly ash into high-purity polyethylene foil envelopes using a microbalance. The foils were folded and placed in 1-mL polyethylene irradiation vials. The elemental standards (50–100 mg weights) used were NBS SRM 1632, 1633, and 1571 and the USGS standard rocks granodiorite GSP-1 and dunite DTS-1, as shown in Table I. These standards were chosen because elemental contents were certified (for NBS Standards) or because good consensus values were available (9, 10).

Samples and standards were irradiated in the Washington State University TRIGA III-fueled research reactor at a thermal neutron flux of 6×10^{12} neutrons $\text{cm}^{-2} \text{s}^{-1}$. The nuclides measured, irradiation times, and counting times were similar to those published previously (17, 18).

All nuclides were quantified by Ge(Li) γ -ray spectroscopy using a Nuclear Data ND 6620 spectrometer system. Reduction of γ -ray peak areas to elemental concentrations was carried out by FOURIER and SPANAL, WSU modifications of the GAMANAL program, using the WSU Amdahl 470 computer (18). Corrections for decay during counting for ^{28}Al , ^{27}Mg , ^{51}Ti , ^{49}Ca , and ^{52}V were made by the method of Hoffman and Van Camerik (19). Corrections for blank values (polyethylene vials and polyethylene envelopes) were made where appropriate (17).

The method for the determination of Fe, Co, Cr, Ni, Cs, Ba, REE (rare earth elements), Sc, Th, Hf, and Ta in the USGS BCR-1 (0.133–7.011 mg) and pottery standard, SP (0.131–1.034 mg), by INAA was similar to that of Davis et al. (20).

RESULTS AND DISCUSSION

Table II shows trace element data obtained for five replicate analyses of SRM 1633a using sample weights of 0.83–5.45 mg. Included for comparison are data for larger samples of SRM 1633 (19.3–20.3 mg) and SRM 1632 (30.1–30.2 mg). Values for the expected relative standard deviation for a single value, $S_c(\%)$, calculated from Poisson counting statistics, are also shown in Table II. Agreement between mean concentrations and reference values is generally within 2 experimental standard deviations.

The SRM 1632 coal is the most heterogeneous standard analyzed because most trace elements are concentrated in mineral species (sulfides, oxides, silicates) rather than in the organic maceral major component. Table II shows that relative standard deviations greater than 20% are observed for

Table II. Measured Elemental Concentrations ($\mu\text{g g}^{-1}$) in NBS Coal (SRM 1632) and Coal Fly Ash (SRM 1633 and 1633a) Standards

element	1633a				1633				1632			
	ref value ^a	mean ^c	rel std dev ^c	$S_c(\%)^d$	ref value ^a	mean ^c	rel std dev ^c	$S_c(\%)^d$	ref value ^a	mean ^c	rel std dev ^c	$S_c(\%)^d$
Ti	0.81 ^b	0.900 ^b	16	16		<i>e</i>				<i>e</i>		
Al	14.4 ^b	16.5 ^b	9.1	6.6		<i>e</i>				<i>e</i>		
Ca	1.11 \pm 0.01 ^b	1.23 ^b	13	19		<i>e</i>				<i>e</i>		
K	1.88 \pm 0.06 ^b	1.77 ^b	13	0.8	1.69 ^b	1.76 ^b	11	2.0	0.281 ^b	0.304 ^b	7.6	1.3
Fe	9.40 \pm 0.10 ^b	8.40 ^b	1.2	0.3	6.14 ^b	6.35 ^b	1.9	0.6	0.87 \pm 0.03 ^b	0.830 ^b	7.2	0.7
V	289	344	8.7	9.0		<i>e</i>				<i>e</i>		
Mn	210	167	4.2	2.3		<i>e</i>				<i>e</i>		
Co	43	39	5.1	0.4	40	38	2.6	0.6	5.6	5.8	10	0.8
Cr	196 \pm 6	190	4.2	0.4	131 \pm 2	124	7.3	0.4	20.2 \pm 0.5	18.3	10	0.8
Ni	127 \pm 4	97	37	7.5	98 \pm 3	121	17	5.5	15 \pm 1	20	55	10
Ga	55	45	11.1	3.3	42	45	18	3.0	5.8	5.8	8.6	3.2
As	145 \pm 15	147	9.5	0.8	61 \pm 6	63	6.4	0.6	5.9 \pm 0.6	6.3	4.8	0.8
Sb	7.1	6.9	10	3.2	6.8	6.6	4.6	2.3	3.5	2.6	140	2.4
Se	10.3 \pm 0.6	13	23	3.3	9.4 \pm 0.5	10.7	3.7	3.3	2.9 \pm 0.3	3.1	9.7	3.8
Rb	131 \pm 2	170	18	2.9	115	136	4.4	3.8	20	23	17	4.8
Cs	10	11	10	1.3	8.6	8.3	8.4	0.9	1.52	1.6	6.7	1.6
Sr	830 \pm 30	790	10	3.6	1380	1460	19	1.7	145	171	13	4.2
Ba	1400	1400	26	4.2	2700	2800	2.1	1.4	330	320	24	2.5
La	83	89	5.6	0.7	79	83	1.2	0.3	10.4	11	8.3	0.6
Sm	17	15	6.7	0.5	12.7	13	10	0.2	1.58	1.8	4.0	0.2
Eu	3.5	3.7	15	1.5	2.6	2.6	9.2	1.0	0.36	0.39	11	2.1
Ce	175	180	11	0.2	149	152	8.6	0.2	21	19	3.7	0.4
Tb	2.4	4.7	37	2.7	1.8	1.7	48	2.0	0.27	0.29	28	4.1
Sc	38	37	5.4	0.2	26.6	30	7.4	0.2	3.78	4.1	9.4	0.2
Th	24.6	24	8.3	0.3	24.6	23	8.6	0.2	3.2	2.9	7.2	0.5
U	10.2 \pm 0.1	8.9	7.9	14		<i>e</i>			1.4 \pm 0.1	1.4	28	11
Hf	7.2	7.0	8.6	1.0	7.6	7.5	5.2	0.6	0.98	0.91	17	1.6
Ta	1.9	2.3	8.7	4.1	1.91	1.84	4.9	2.4	0.25	0.24	12	4.2

^a Reference value: NBS Certified for mean \pm standard deviation values. All others are taken from Gladney et al. (9). ^b Value for element is in percent; all others are in $\mu\text{g g}^{-1}$. ^c Mean and relative standard deviation computed from replicates: for 1633a, four replicates of 830 μg , 950 μg , 1130 μg , and 5450 μg (except for Ti, Al, Ca, V, Mn, As, Ga, La, K, and Sm for which fifth sample of 4940 μg was used). For 1633, four replicates of 19.3, 20.1, 20.2, and 20.3 mg were used. For 1632, four replicates of 30.1, 30.1, 30.1, and 30.2 mg were used. ^d $S_c(\%)$ expected relative standard deviation of single value calculated from counting statistics. ^e Element not determined.

Sb, Ni, Ba, U, Zr, and Tb, and that these values are much larger than the expected counting statistics relative standard deviations, $S_c(\%)$. The large relative standard deviations for these elements are much higher than the range of relative standard deviations for the other elements (3.7–17%) and are thus not representative of overall analytical precision but are probably a result of sample heterogeneity. If an element is present as a discrete trace mineral species (or is concentrated in a minor mineral component), A, of the coal and if all other components can be classed as barren component B, then from eq 1 $C_A f_A = C$, $d_B = d$, and $f_B = 1$. Thus, the sampling error, $S(\%)$, is given by

$$S(\%) = 100 \left[\frac{d_A}{f_A} \frac{4\pi^3}{3} \frac{1}{W} \right]^{1/2} \quad (2)$$

Table III shows values of $S(\%)$ calculated from eq 2 assuming that the mineral species of Sb, Ba, Zr, Ni, and Fe in the coal are stibnite, Sb_2S_3 , barite, BaSO_4 , zircon, ZrSiO_4 , millerite, NiS , and pyrite, FeS_2 , respectively. These are probable species (21) but $S(\%)$ values calculated for other discrete mineral forms of these elements are not significantly different from those in Table III. The very large calculated sampling error for Sb, 166%, explains the large observed analytical error. Calculations of the sampling constant for Sb, K_s (weight in grams to obtain 1% sampling error), as defined by Ingamells and Switzer (22) gives a value of 588 g for the NBS coal. Previous workers (23) have demonstrated the heterogeneity of SRM 1632 for Sb using the recommended sample size of 0.250 g. Sampling error also appears to explain the large relative standard deviations for Ba, Zr, and for U, if considered a constituent of zircon in the coal. The elements

Table III. Sampling Error for NBS SRM 1632 for Sb, U, Ni, Ba, Zr, and Fe, As, Cr, Co, Se

element	assumed form ^a	calcd $S(\%)^b$	obsd rel std dev ^c
Sb	Sb_2S_3	166	140
Ba	BaSO_4	13	24
U	ZrSiO_4	36	28
Zr	ZrSiO_4	36	32
Ni	NiS	62	55
Fe	FeS_2	2.45	7.2
As	FeS_2	2.45	4.8
Cr	FeS_2	2.45	10
Co	FeS_2	2.45	10
Se	FeS_2	2.45	9.7

^a Element assumed present only in species indicated. ^b Calculated from eq 2. ZrSiO_4 $d_A = 4.56 \text{ g cm}^{-3}$; BaSO_4 $d_A = 4.57 \text{ g cm}^{-3}$; NiS $d_A = 5.4 \text{ g cm}^{-3}$; FeS_2 $d_A = 5.0 \text{ g cm}^{-3}$; Sb_2S_3 $d_A = 4.6 \text{ g cm}^{-3}$; $W = 0.0300 \text{ g}$. $f = 2.5 \times 10^{-3} \text{ cm}$. ^c Sample weights used: 30.1, 30.1, 30.1, 30.2 mg.

As, Cr, Co, and Se are often associated with pyrite, FeS_2 , which is normally the major Fe species in bituminous coals (21). Assuming all Fe is present as FeS_2 and that this is the major host for As, Cr, Co, and Se, the calculated $S(\%) = 2.45\%$ for these elements shows that heterogeneity is a minor contributor to the analytical precision. Similarly, sampling error is likely to be a small contribution to overall error for elements, such as Al, K, Rb, Cs, etc., distributed in the abundant clay fraction of the coal.

The data for NBS SRM 1633 using sample weights in the range 19.3–20.3 mg (Table II) show that except for Tb, all relative standard deviations are $\leq 20\%$, with 19 elements having relative standard deviations $\leq 10\%$. Thus SRM 1633

Table IV. Measured Elemental Concentrations ($\mu\text{g g}^{-1}$) in U.S. Geological Survey Basalt Standard, BCR-1, and Standard Pottery, SP

element	BCR-1				SP			
	ref value ^a	mean ^c	rel std dev ^c	$S_c(\%)^d$	ref value ^e	mean ^c	rel std dev ^c	$S_c(\%)^d$
Na	2.43 ^b	2.31 ^b	7.1	0.2	0.258 ^b	0.27 ^b	16	3.5
K	1.40 ^b	1.37 ^b	14	3.6	<i>f</i>	<i>f</i>		
Fe	9.38 ^b	9.41 ^b	4.5	0.2	<i>f</i>	<i>f</i>		
Al	7.21 ^b	7.07 ^b	3.0	0.6	15.8 ^b	16.7 ^b	8.4	1.2
Ti	1.33 ^b	1.24 ^b	8.2	3.0	0.79 ^b	0.83 ^b	10	7.8
Mg	2.08 ^b	2.05 ^b	18	5.3	<i>f</i>	<i>f</i>		
Ca	4.97 ^b	4.56 ^b	9.1	2.9	<i>f</i>	<i>f</i>		
V	404	378	5.0	1.8		158	12	7.5
Mn	1410	1250	9.1	1.6	40.9	42	17	0.7
Co	36.3	38.4	2.6	0.1	<i>f</i>	<i>f</i>		
Cr	16	16.2	22	1.3	<i>f</i>	<i>f</i>		
Ni	13	32.8	40	10	279	287 ^g		
Cs	0.97	0.99	6.5	1.7	<i>f</i>	<i>f</i>		
Ba	678	716	13	2.7	<i>f</i>	<i>f</i>		
La	25.0	25.5	2.4	0.4	44.9	45.4	10	1.1
Ce	53.7	53.3	2.6	0.2	803	80.8	2.4	0.2
Nd	28.7	25.4	12	8.5		33.6	5.1	6.7
Sm	6.58	6.61	4.5	0.1	5.78	5.80	3.5	0.1
Eu	1.96	1.96	2.6	0.8	1.45	1.32	11	0.7
Tb	1.05	0.99	5.4	1.3		0.67	4.5	2.8
Dy	6.35	6.0	25	2.1	4.79	4.85	7.0	4.0
Ho	1.25	1.54	33	6.7		1.05	3.8	19
Tm	0.59	0.56	2.7	1.2		0.42	20	2.5
Yb	3.34	3.50	11	1.3	2.80	2.60	6.2	1.2
Lu	0.51	0.51	9.7	0.9	0.40	0.45	13	1.0
Hf	4.90	4.95	5.7	0.3	<i>f</i>	<i>f</i>		
Zr	191	178	8.4	7.9	<i>f</i>	<i>f</i>		
Ta	0.79	0.71	4.1	1.9	<i>f</i>	<i>f</i>		
Th	6.04	5.99	10	0.5	<i>f</i>	<i>f</i>		

^aConsensus values from Gladney and Burns (10). ^bValue for element is in percent; all others are in $\mu\text{g g}^{-1}$. ^cMeans and relative standard deviations calculated from replicate analysis: for BCR-1, 133.2, 150.5, 344.3, 966.4, and 7011 μg (except for Na, Ti, Al, Mg, V, Ca, Dy, and Mn for which six replicates were used in the range 174.5–791.2 μg); for SP, 185.1, 196.6, 208.8, 257.3, 546.2, and 969.6 μg (except for Na, Al, Ti, V, Mn, and Dy for which seven replicates were used in weight range 130.8–1034 μg). ^d $S_c(\%)$: expected relative standard deviation of single value calculated from counting statistics. ^eData from Perlman and Asaro (16). ^fNot determined. ^gSingle determination.

is sufficiently homogeneous for 20 mg sample weights for these elements and can confidently be used at less than the NBS recommended weight of 250 mg. The data for SRM 1633a (Table II) for much lower sample weights (0.83–5.45 mg) show that relative standard deviations >20% are observed for Ni, Se, Ba, and Tb but that Al, Fe, V, Mn, Co, Cr, Ga, As, Sb, Cs, Sr, La, Sm, Sc, Th, U, Hf, and Ta have relative standard deviations $\leq 10\%$. The poor precision for Ni, Se, and Ba is not a lack of analytical sensitivity as shown by the $S_c(\%)$ data but probably reflects sample heterogeneity. The poor precision for Tb in 1633a contrasts with good precision for the other REE and is thus unlikely to be heterogeneity. Coal fly ashes of particle size <170 mesh (<88 μm diameter) consist primarily of glass cenospheres, and mullite crystals, $3\text{Al}_2\text{O}_3\text{--}2\text{SiO}_2$, with minor amounts of a magnetic component, either a ferrite or magnetite (24, 25). Lyon (25) has shown that most trace elements are primarily associated with the glass material but that Fe, V, Cr, Mn, and Ni are partially associated with the magnetic component. Segregation of a magnetic component does not appear to be the reason for the poor precision for Ni (38% RSD) because good reproducibility is obtained for Fe, Mn, Co, and Cr. The poor precision for Ba (26%) probably results from the occurrence of a Ba feldspar as a minor phase in the fly ash as reported by Korotev and Lindstrom (15).

Table IV shows trace element data obtained on 0.133–7.011 mg samples of USGS BCR-1 and on 0.185–1.034 mg samples of standard pottery, SP. For BCR-1, the recent data tabulation of Gladney and Burns (10) was used for reference values and the original data of Perlman and Asaro (16) are quoted for SP. Good agreement with the consensus values of Gladney

and Burns (10) is indicated for BCR-1. The relative standard deviations for BCR-1 constituents are $\leq 20\%$ for all elements except Cr, Ni, Dy, and Ho. The poor precision for Dy and Ho is difficult to explain by sample heterogeneity because the other REE show excellent precision. The consensus values for Ni and Cr tabulated by Gladney and Burns (10) also show large relative standard deviations of 31% and 25%, respectively; these elements may be associated with a minor mineral in BCR-1, e.g., chromite or olivine, although Cr and Ni are not correlated in the data set. The more limited data available for pottery SP make this material less useful than NBS or USGS materials as a trace element standard, but the uniform matrix, indicated by the excellent reproducibility for the 16 elements measured (Table III) make it useful for QC purposes.

Registry No. Ti, 7440-32-6; Al, 7429-90-5; Ca, 7440-70-2; K, 7440-09-7; Fe, 7439-89-6; V, 7440-62-2; Mn, 7439-96-5; Co, 7440-48-4; Cr, 7440-47-3; Ni, 7440-02-0; Ga, 7440-55-3; As, 7440-38-2; Sb, 7440-36-0; Se, 7782-49-2; Rb, 7440-17-7; Cs, 7440-46-2; Sr, 7440-24-6; Ba, 7440-39-3; La, 7439-91-0; Sm, 7440-19-9; Eu, 7440-53-1; Ce, 7440-45-1; Tb, 7440-27-9; Sc, 7440-20-2; Th, 7440-29-1; U, 7440-61-1; Hf, 7440-58-6; Ta, 7440-25-7; Na, 7440-23-5; Mg, 7439-95-4; Nd, 7440-00-8; Dy, 7429-91-6; Ho, 7440-60-0; Tm, 7440-30-4; Yb, 7440-64-4; Lu, 7439-94-3; Zr, 7440-67-7.

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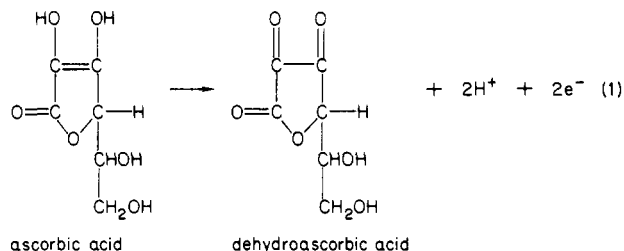
Irreversible Reaction Kinetics of the Aerobic Oxidation of Ascorbic Acid

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Aerobic oxidation of ascorbic acid (AA) is studied at 25, 62, 75, and 86 °C. The AA is determined by 2,6-dichloroindophenol titration and dehydroascorbic acid (DHA) is determined simultaneously by continuous-flow derivatization with o-phenylenediamine using fluorescence detection. The pseudo-first-order, reversible rate constants for the formation of DHA and diketogulonic acid are discussed. The activation energy for AA degradation and the irreversible pseudo-first-order rate constant for AA and DHA loss are presented. A degradation pathway from AA to products without the formation of DHA is postulated.

Ascorbic acid (AA) is an unsaturated lactone which is a strong reducing agent. It is converted to dehydroascorbic acid (DHA) according to the reaction

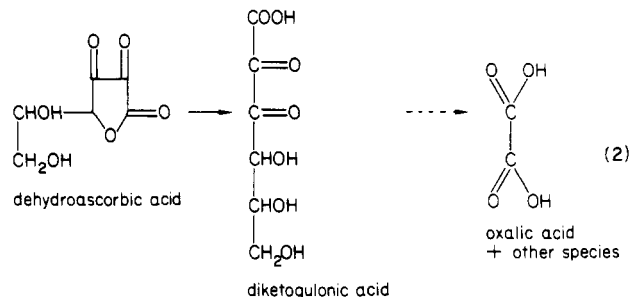


The reaction is apparently not reversible and is a function of at least the temperature, pH, and oxygen content of the aqueous sample. The autooxidation is strongly catalyzed by several metal ions, notably Cu(II) and Fe(III).

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Several mechanistic studies on the oxidation of AA have been performed in the last 50 years. An excellent review of the literature of aerobic and catalyzed oxidation is presented by Mushran and Agrawal (1). Definitive kinetic results may have been unobtainable for several reasons: (1) the presence of metal ions as impurities in laboratory water sufficient to catalyze the reaction, (2) the absence of specific methods for the determination of AA, and (3) the absence of precise and sensitive methods for the determination of DHA.

Whereas under anaerobic conditions AA degrades to furfural and carbon dioxide, the aerobic mechanistic path is postulated to be oxidation to DHA followed by hydrolysis (2).



The degradation is apparently a function of at least the concentrations of the metal ions present, the pH, and the available light (3, 4). The different kinetic routes apparently all produce DHA.

Hence, the oxidation of AA is assumed to occur by the initial formation of DHA followed by conversion of that species to diketogulonic acid (DKA) (5). The reactions are apparently pH dependent. In a more recent study, Blaug and Hajratwala (6) determined the unreacted AA vs. time using the 2,6-dichloroindophenol volumetric determination. An apparent first-order rate of degradation was achieved at 67 °C and a