Substoichiometric Isotope Dilution Analysis of Vanadium by Synergistic Extraction

II. 1 Substoichiometric Isotope Dilution Analysis of Vanadium by Synergistic Extraction

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Substoichiometric isotope dilution methods have the following advantages:[1] (1) Quantitative separation and recovery of an element in question from a matrix are not required, and (2) the element can be determined by measuring only the radioactivity of the substoichiometric extract without any calibration curves. Up to the present, substoichiometric methods of vanadium have not been developed.[2] This may be ascribed to the insufficient information for the separation chemistry of vanadium, particularly for solvent extraction.

We have studied on the extraction of vanadium(IV) and vanadium(V) with some chelating reagents in a series of investigations and found that vanadium(IV) is synergistically extracted with thenoyltrifluoroacetone(HTTA) and trioctylphosphine oxide(TOPO), as $VO(TTA)_2TOPO$. In this report, the substoichiometric extraction of vanadium(IV) with HTTA in the presence of an excess of TOPO is investigated and applied to the determination of vanadium in NBS SRM-1633 coal fly ash.

The radioisotope, ^{48}V, was produced from titanium with 18 MeV protons in Tohoku University Cyclotron and Radioisotope Center. Carrier free ^{48}V was separated by diethyldithiocarbamate extraction under suitable conditions[3] after the titanium target was dissolved in dil. sulfuric acid. The radioactive vanadium(IV) standard solution was prepared by mixing a known quantity of vanadium (V) carrier and ^{48}V and reducing them with a sodium hydrogen sulfite solution. Other materials and apparatus were the same as those previously.[4]

A 5-ml portion of 2×10^{-4} M vanadium(IV) solution containing $(1\text{-}2)\times10^{-3}$ M ascorbic acid and 0.01 M acetate buffer(pH3-6) was placed in a 30-ml centrifuge tube with a fitted cap. A 5-ml portion of a cyclohexane solution containing a substoichiometric amount(2×10^{-4} M) of HTTA and an excess of TOPO(1×10^{-2} M) was added and the contents were shaken for 30 min. The γ-activity of a 3-ml portion of the organic phase was measured.

The pH region in which a constant amount of vanadium(IV) is extracted with a substoichiometric amount of HTTA is shown in Fig. 1. The equilibrium for the substoichiometric extraction is attained by shaking for over 30 min. Quantitative reaction of HTTA of the substoichiometric reagent is achieved at pH 3.9-4.9. In this region, precision of the substoichiometric extraction is of 0.75 % as the relative standard deviation(RSD) of the activity measurement.

A substoichiometric extraction with 2.0×10^{-4} M HTTA in the presence of 1.0×10^{-2} M TOPO was applied to a series of solutions containing varying amounts of vanadium(IV) labeled with ^{48}V. As shown in Fig. 2, the radioactivity of the organic phase increases with increase in the amount of vanadium(IV) up to the point corresponding to a vanadium(IV):HTTA ratio of 1:2. Beyond this point,

i.e., under the substoichiometric conditions, a constant amount of vanadium(IV) is extracted with HTTA. The reproducibility of the substoichiometric extraction with 2.0×10^{-4} and 1.0×10^{-4} M HTTA is as good as 1.0 and 0.7 % respectively.

Some metal ions such as iron(III), hafnium(IV), and niobium(V) were found to strongly interfere the extraction of a constant amount of vanadium(IV) with the substoichiometric amount of HTTA. Hence, pre-separation methods of vanadium were considered by using two extractants, i.e., benzoylphenylhydroxylamine(BPHA)[5] and DDC. Vanadium(V) is extracted with BPHA in benzene from 3-5 M hydrochloric acid solutions and back-extracted with ascorbic acid in 2 M sulfuric acid by reducing to vanadium(IV). Foreign metal ions are extracted again with BPHA under the same conditions, while vanadium(IV) remains in the aqueous phase. Then vanadium(IV) is isolated by DDC extraction described above. Vanadium may be separated from almost all other metals by this method.

The accuracy and precision of the method should be evaluated by determining vanadium in the presence of large amounts of interfering metals. The analytical results for the synthetic mixture containing a known amount of vanadium are shown in Table 1. The mean value of 412 μg agrees well with the amount taken, the precision being also satisfactory. No interference is found even for the elements which may be difficult to be completely separated from vanadium.

The method is accurate, precise, and applicable to practical samples such as the standard reference materials, NBS coal fly ash. The analytical results are shown in Table 2 in which vanadium(IV) is substoichiometrically extracted in twice with a constant amount of HTTA and TOPO from the same test solution.(it is expressed as the number of extraction in this table) Since the results obtained from the two substoichiometric extractions are well consistent, no interference with other metals can be considered. The determined value, 223±4 μg/g, is good agreement with the NBS certified value, 214±8 μg/g. The present method can be applied to various samples containing vanadium in moderate levels.

References

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Table 1. Determination of vanadium in the synthetic mixture

Vanadium taken μg	Other ions added mg	Vanadium (V-48) spiked(M_s) μg	Activity from spike solution(a_s) cpm	Activity from test solution(a) cpm	Vanadium* found (M) μg
413.6	Fe; 50.3 Ti; 9.0 Zr; 0.50 Mo; 0.05 Nb; 0.05 Hf; 0.05	310.2	20531	8904	405.1
				8860	408.6
				8670	424.4
				8841	410.2

Mean ±σ = 412.1±8.5 μg, RSD = 2.1 %, deviation from the amount of vanadium taken = - 0.36 %.

*Calculated from $M = M_s(a_s/a - 1)$.

Table 2. Determination of vanadium in NBS SRM-1633, coal fly ash

Sample taken g	Vanadium (V-48) spiked μg	Activity from spike solution cpm	Number of extraction	Activity from test solution cpm	Vanadium found μg	Concentration μg/g
1.0071	$206._8$	23804	1	11625	$216._6$	$215._1$
			2	11367	$226._3$	$224._7$
			1	11484	$221._8$	$220._3$
			2	11413	$224._5$	$222._9$
1.0130	$258._5$	21239	1	11320	$226._5$	$223._6$
			2	11297	$227._5$	$224._6$
			1	11255	$229._3$	$226._4$
			2	11350	$225._2$	$222._3$

Mean $\pm\sigma = 222._5 \pm 3.5$ μg/g, RSD = 1.6 %.
NBS certified value = 214 ± 8 μg/g.

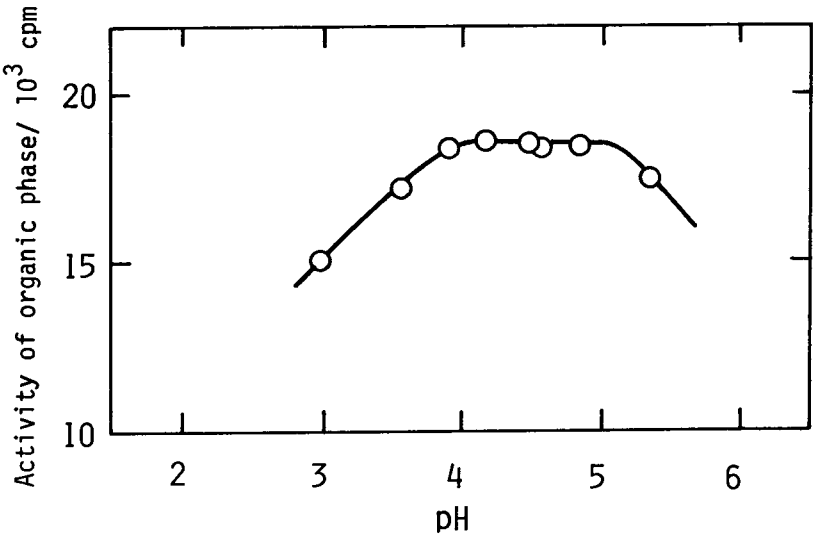

Fig. 1. Effect of pH on the substoichiometric extraction of vanadium(IV). [V(IV)] = 2.0×10^{-4} M, [HTTA] = 2.0×10^{-4} M, [TOPO] = 1.0×10^{-2} M, shaking time: 30 min.

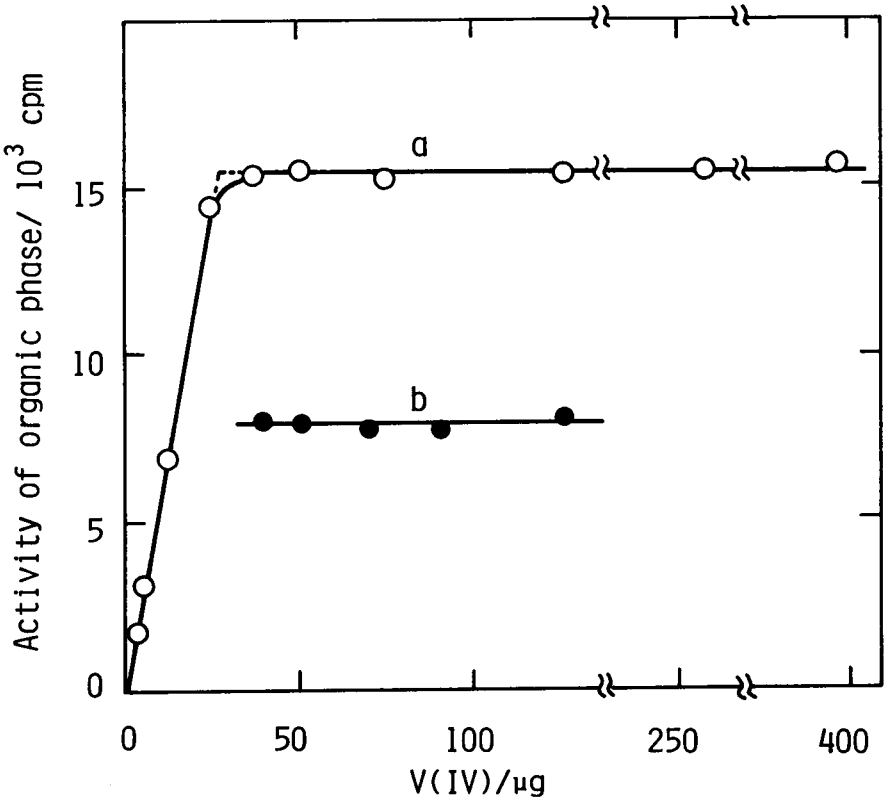

Fig. 2. Reproducibility of the substoichiometric extraction of vanadium(IV). [TOPO] = 1.0×10^{-2} M, pH 4.4-4.7, shaking time: 30 min. a; [HTTA] = 2.0×10^{-4} M, b; [HTTA] = 1.0×10^{-4} M.