

SENSITIVITY INCREASE OF ATOMIC ABSORPTION ANALYSIS OF VANADYL ION
BY APPLYING PRE-ELECTROLYSIS

Mitsutaka KITAMURA, Kazuo YAMASHITA, and Hideo IMAI
Faculty of Integrated Arts and Sciences, Hiroshima University, Hiroshima
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The sensitivity increase of atomic absorption analysis for vanadyl ion by applying pre-electrolysis is described. It is shown that pre-electrolysis results in V-O bond breaking and facilitates free atom population in flame.

The application of atomic absorption analysis for stable metal monoxide molecules is limited owing to meager free atom population in flame. Willis¹⁾ recommended the use of highly reducing nitrous oxide-acetylene flame for refractory metals. Recently Musha²⁾ investigated details of the mechanism that VO species react with the reducing fragments, NH, CN, and C, as follows;



On the other hand, in our previous report³⁾ it was shown that the irreversible electrode process of vanadyl ion involves the breaking of V-O bond. Therefore, it can be expected that the pre-electrolysis will increase the free atom population in flame even in weakly reducing media. The effect was found to be noticeable in a rather high concentration range of VO^{2+} .

Procedures: The solution of VO^{2+} were prepared by dissolving vanadyl sulfate in 0.05 M sulfuric acid or dissolving vanadyl acetylacetonate in acetonitrile(AN) containing 0.1 M tetraethylammonium perchlorate(TEAP) and acetylacetone added in excess by ten times equivalents of the vanadyl ion. The concentration of oxovanadium(IV) ranges from 1 to 50 ppm. The controlled-potential electrolysis was carried out in an H type cell with mercury pool as a cathode. Purified nitrogen was passed through the solution during the electrolysis and the applied potential was controlled at -1.15 V vs. S.C.E. in the case of aqueous solution and at -2.10 V vs. $\text{Ag}/0.01 \text{ M AgClO}_4$ in the case of AN solution. After the electrolysis was completed (approximately in 30 min.), the solution was supplied to atomic absorption analysis. Composition of the flame was controlled by nitrous oxide flow rate of 7.0 l/min under the pressure of 1.5 Kg/cm^2 and acetylene flow rate of 6.0 l/min under the pressure of 0.5 Kg/cm^2 . (Note that Nakahara et al.⁴⁾ recommended the use of much higher flow rate of nitrous oxide. In our experiment an oxidizing flame such as acetylene-air flame could not be used even by applying pre-electrolysis. At least a reducing environment is necessary in order to prevent oxidation in flame.) The spectrophotometry was carried out at the wave length of 318.40 nm.

Results: Typical polarograms obtained are shown in Fig. 1, in which (A) and (B) represent the case of the aqueous solution of vanadyl sulfate and AN solution of vanadyl acetylacetonate, respectively. In both cases a solid line illustrates a

current-potential curve for the solution before electrolysis and a dotted line after electrolysis. The reduction product in (A) is V^{2+} ion⁵⁾ and that in (B) $[V(acac)_3]^-$ ion³⁾. Fig. 2 shows the working curves of the atomic absorption analysis for both cases of (A) and (B). The plots of absorbance against concentration of vanadyl sulfate for aqueous solution without electrolysis deviate from the linearity at concentrations higher than 20 ppm. The effect of pre-electrolysis is noticeable at concentrations higher than 20 ppm (Fig. 2 (A)), the absorbance being linearly proportional

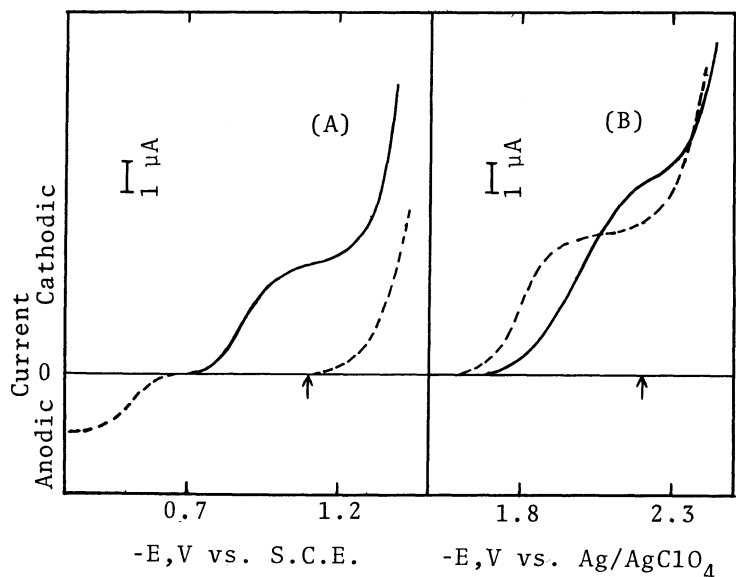


Fig. 1. Current-potential curves. $[VO_2^{2+}] = 50$ ppm, (A); aqueous solution (B); acetonitrile solution, — before and --- after electrolysis at constant potential shown by \uparrow .

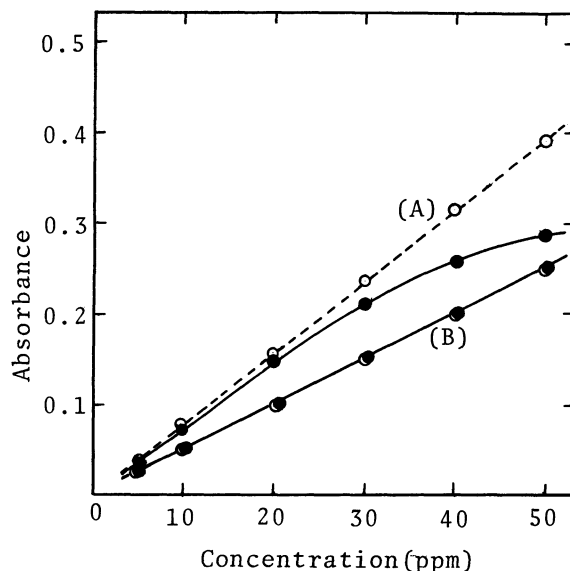


Fig. 2. Working curves of the atomic absorption analysis for both cases of (A) and (B). --O-- with pre-electrolysis —●— without pre-electrolysis

to the concentration of vanadium in the range from 1 to 50 ppm. This result can be interpreted by an increase of free atom population due to the breaking of V-O bond by pre-electrolysis. On the other hand, the effect of pre-electrolysis could hardly be observed for the AN solution as shown in Fig. 2 (B), plots of absorbance vs. concentration indicating no difference with and without pre-electrolysis. In this solution abundant CN fragments may be supplied from AN molecules in the flame, where the highly reducing environment is furnished and metal monoxide can be partially reduced. As a conclusion it is noticed that the sensitivity of atomic absorption analysis for vanadyl ion in an aqueous solution can be increased by the pre-electrolysis, even in a weakly reducing flame. This pre-treatment seems to be promising not only for vanadyl ion but also for the other refractory metals such as U, Zr, Ti, etc. The details of this investigation will be published in the future.

References

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