

## Note on automated spectrophotometric set-point titrations of submicromole amounts of Ca<sup>2+</sup> and Zn<sup>2+</sup>

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## Note on Automated Spectrophotometric Set-Point Titrations of Submicromole Amounts of $\text{Ca}^{2+}$ and $\text{Zn}^{2+}$

W. Smit and H. N. Stein

Laboratory of General Chemistry,  
Eindhoven University of Technology, Eindhoven,  
The Netherlands

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*Notiz über automatisierte spektralphotometrische Titrationen submikromolarer Mengen von  $\text{Ca}^{2+}$  und  $\text{Zn}^{2+}$  bis zum vorgewählten Endpunkt*

Best. von Calcium, Zink; Spektralphotometrie, Volumetrie; vorgewählter Endpunkt, systematische Fehler

From the results of our set-point titrations of calcium and zinc with an automatic titrator after Slanina *et al.* [2], which drives a Metrohm E457-0.5 ml microburette, we conclude that considerable systematic errors result when the true strength of the titrant is taken into the calculation of the cation concentration.

These systematic errors, which cannot be inferred from Slanina's [2] results, are already evident from the deviating results, obtained when the spectrophotometer is set to measure the absorption either of the free indicator (I) (calcein:  $\lambda = 510$  nm, xylenol orange:  $\lambda = 427$  nm) or of the metal-indicator complex (MI) ( $\text{Ca}^{2+}$ :  $\lambda = 486$  nm,  $\text{Zn}^{2+}$ :  $\lambda = 570$  nm).

Titrations with about 1  $\mu\text{g}$  of cation present show differences of 10% and 2% for the calcium and zinc titrations, respectively. The macro-scale titration value lies between those of the MI and I titrations, but is nearer to the MI titration value. From an adaptation of the theoretical to the experimental titration curve (compare Kragten [1]) we estimated the intrinsic systematic error as +0.5% in the consumption of

EGTA solution in case of the calcium I titration and +1.0% in case of the calcium MI titration. The greater part of the systematic error originates from dilution upon sample and titrant introduction.

Our experimental results show that set-point titrations can give reproducible results both in a series in one titration solution and when the titration series is repeated in a fresh titration solution under exactly the same conditions of dilution, set-point, indicator concentration, etc. as before. The systematic error can be eliminated by performing the standardization of the titrant with a standard metal salt solution under the same conditions as in the actual titration. The condition of equal dilution can easily be fulfilled by co-injection of such a volume of solvent that

$$\begin{aligned} V'_{\text{sample}} + V'_{\text{titrant}} \\ = V_{\text{sample}} + V_{\text{titrant}} + V_{\text{solvent}} \end{aligned}$$

where the terms on the left hand side refer to the standardization experiment.

The method can safely be used to determine small concentration differences between two solutions, as is the case in adsorption experiments. The employment of an automatic titrator is convenient but not essential for the method.

Our experience is that manual performing of the titrations does not entail much loss of rapidity when a digital photometer and a Metrohm micro-hand burette are employed.

### References

1. Kragten, J.: *Talanta* **18**, 311 (1971)
2. Slanina, J., Vermeer, P., Mook, G., Reinders, H. F. R., Agterdenbos, J.: *Z. Anal. Chem.* **260**, 354 (1972)

Dr. W. Smit, Technological University, Lab. for General Chemistry, Eindhoven, The Netherlands