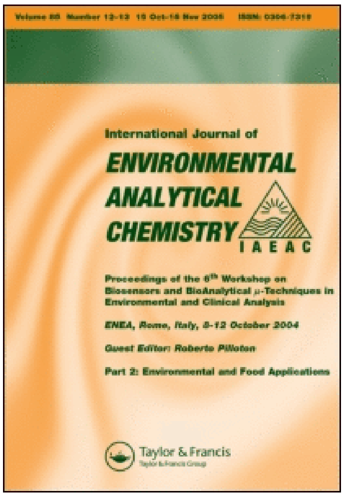

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Comparison of Procedures for the Determination of Silicon in Atmospheric Particulate Matter

B. R. Appel[a]; E. M. Hoffer[a]; M. Haik[a]; D. Levaggi[a]; A. Del Rosario[a]; H. Moore[a]; S. Twiss[a]; P. K. Mueller[a]
[a] Air and Industrial Hygiene Laboratory, Laboratory Program, State of California Department of Health, Berkeley, California, U.S.A.

To cite this Article Appel, B. R. , Hoffer, E. M. , Haik, M. , Levaggi, D. , Rosario, A. Del , Moore, H. , Twiss, S. and Mueller, P. K.(1976) 'Comparison of Procedures for the Determination of Silicon in Atmospheric Particulate Matter', International Journal of Environmental Analytical Chemistry, 4: 3, 197 — 203

To link to this Article: DOI: 10.1080/03067317608071114

URL: http://dx.doi.org/10.1080/03067317608071114

Intern. J. Environ. Anal. Chem., 1976, Vol. 4, pp. 197–203

Printed in Great Britain

Comparison of Procedures for the Determination of Silicon in Atmospheric Particulate Matter

B. R. APPEL, E. M. HOFFER, M. HAIK, D. LEVAGGI,†
A. DEL ROSARIO, H. MOORE, S. TWISS and P. K. MUELLER

Air and Industrial Hygiene Laboratory, Laboratory Program,
State of California Department of Health, 2151 Berkeley Way,
Berkeley, California 94704, U.S.A.

(*Received January 24, 1975*)

KEY WORDS: Silicon, atmosphere particulate matter, NBS standard reference materials, lithium metaborate.

Flame atomic absorption photometry (AA), and emission spectroscopy (ES) were compared to the molybdenum blue spectrophotometric method (SP) for analysis of silicon in atmospheric particulate matter and in NBS standard reference materials. All techniques gave systematically low values, the range being 9–30% low with respect to the NBS values. Employing lithium metaborate as the fusion medium, the AA method proved to be approximately equivalent to the SP procedure in precision and accuracy. The ES technique displayed relatively poor accuracy and precision. Lithium metaborate provided substantially better solubilization of the more refractory NBS standards compared to sodium carbonate.

INTRODUCTION

The identification of sources of atmospheric particulate matter has been the subject of a number of recent studies.[1,2,11,12] Such identification is often based upon analysis for characteristic elements. For example, the contribution from marine aerosols is often inferred from the sodium content and the contribution from soil, by the amount of silicon.

X-ray fluorescence techniques can provide rapid determination of silicon in atmospheric particulate samples. However, the low energy of the Si X-ray with consequent likelihood of errors from self-absorption has dimin-

---

†Bay Area Air Pollution Control District, 939 Ellis Street, San Francisco, California 94109.

ished the usefulness of this technique. A more suitable technique for silicon analysis employed heretofore by our laboratories involves ashing and alkaline fusion to form water soluble silicates. These are reacted with ammonium molybdate, reduced to molybdenum blue and determined by absorption spectrophotometry.[3,10] The lower limit of detectability for Si by this method was found to be about 0.5 μg which is quite adequate for many atmospheric particulate samples. However, the spectrophotometric procedure is time-consuming, requiring about 4 days for a batch of 25 samples. Therefore, the precision and accuracy of alternate and potentially more efficient techniques were explored.

The present paper presents a comparison of results obtained by flame atomic absorption photometry (AA), emission spectroscopy (ES), and the spectrophotometric method (SP) which is considered the reference technique. The comparison employs both atmospheric particulate matter samples and NBS standards.

TABLE I
NBS standard reference materials

Composition	NBS Number	% Si
Sodium feldspar	99a	30.5
Flint clay	97a	20.4
Cement	1013	11.3
Cement	1015	9.65
Chrome refractory	103a	2.16
Burned magnesite	104	1.19

EXPERIMENTAL

Twenty-four atmospheric particulate matter samples were collected on Whatman 41 8 × 10″ cellulose filters using conventional Hi-Volume samplers. Twenty-four samples were collected, the ashed samples homogenized and portions taken for SP, ES and AA analysis. Samples for SP analysis were solubilized by fusion with NaOH in nickel crucibles while those for AA analysis employed Na_2CO_3 in platinum crucibles. Samples for ES did not require such fusion. Usually one determination of these samples was reported by each technique. However, duplicate determinations were obtained for a sub-set by the SP method.

Six NBS standard reference materials were also analyzed, as listed in Table I, covering the compositional range of 1 to 30% Si. Each standard was prepared as eight samples. The resulting 48 samples submitted for such analysis were coded and randomized to minimize analytical bias.

The procedures employed for fusion of the NBS standards differed somewhat from conditions employed with the atmospheric samples; prior to SP analysis the NBS materials were fused with Na_2CO_3. In some cases SP analysis was repeated employing lithium metaborate fusion.[4-9] In the AA analysis, lithium metaborate fusion was employed. In all cases, samples were heated to fusion over a Meker burner. While lacking temperature control this yielded lower contamination of samples compared to the furnace in common use for general laboratory applications.

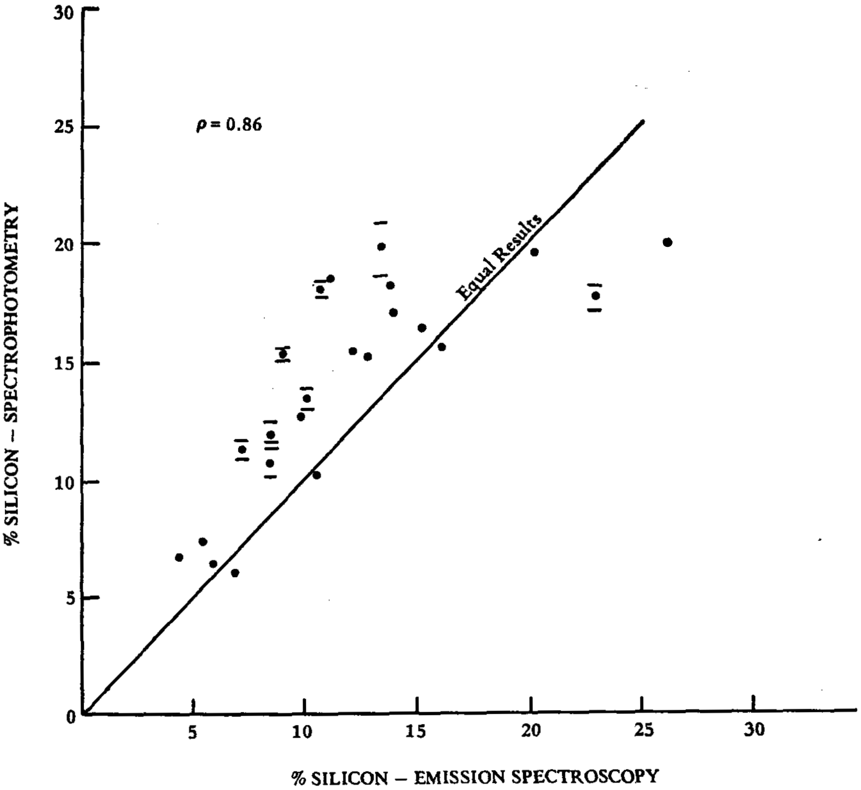

FIGURE 1 Silicon analysis of particulate matter samples by spectrophotometry and emission spectroscopy.

Emission spectra were obtained on a Jarrell-Ash 3.4 meter emission spectrograph using D.C. arc excitation. Ash samples were diluted with Li_2CO_3 and a subsample of the Li_2CO_3-ash mixture mixed with a Li_2CO_3-

GeO_2 buffer-internal standard blend. The Si content was determined from the Si/Ge intensity ratio. The minimum detectable Si is about 0.25 μg by this method, but it was not used for quantitative analysis below 1 μg.

AA analyses were obtained with the Perkin-Elmer Models 403 and 304 instruments using an N_2O-acetylene flame, sodium metasilicate solutions as standards with the conventional aspirator technique. The samples analyzed were processed by dissolving the alkaline melts in dilute acid and adjusting to a known volume. The minimum detectable Si by AA was about 2 μg.

RESULTS

Figure 1 is a plot of % Si found in the atmospheric samples as determined by ES and by SP methods. The reproducibility of the latter is indicated by the variability shown for duplicate samples; the average coefficient of variation for the duplicates was 5.3%. The plot shows the line which would correspond to perfect agreement and indicates that the SP method results tend to be higher than those by ES. The correlation coefficient for the two sets of data is 0.86 and the median ratio of Si by ES:SP is 0.81 with a range from 0.59 to 1.33.

The comparison between AA and the reference method for atmospheric samples is shown in Figure 2. The correlation coefficient between these two sets of data is 0.94 and the median ratio of Si values by AA/SP, 1.01 with a range from 0.74 to 1.17.

Table II details the accuracy and precision of the three methods in the analysis of NBS standard samples. Regarding accuracy, AA gave the best overall recovery, 91% compared to 83% and 70% for SP† and ES, respectively. The precision of the SP,† AA and ES methods, as measured by their pooled standard deviation, was 0.65, 0.70 and 2.41, respectively, indicating much poorer results by the ES method. Employing the F-ratio test for equality of variances, precision by the SP and AA methods were not significantly different while those of the SP and ES methods were not equal.‡

Employing lithium metaborate for SP analysis with samples 99a and 1013 the accuracy of the method was substantially improved over that with sodium carbonate.

DISCUSSION AND CONCLUSIONS

Considering the methods comparison based on atmospheric samples, the degree of agreement between the emission and spectrophotometric or

---

†With sodium carbonate fusion.

‡AA/SP F(42, 40) = 1.16; ES/SP F(42, 40) = 13.7.

reference methods indicates the emission method yields consistently lower results. Between the atomic absorption and spectrophotometric methods, however, the results indicate closer agreement and would justify the analysis of atmospheric samples by this alternate method. Presumably the degree of agreement could be improved still further by use of the same fusion medium.

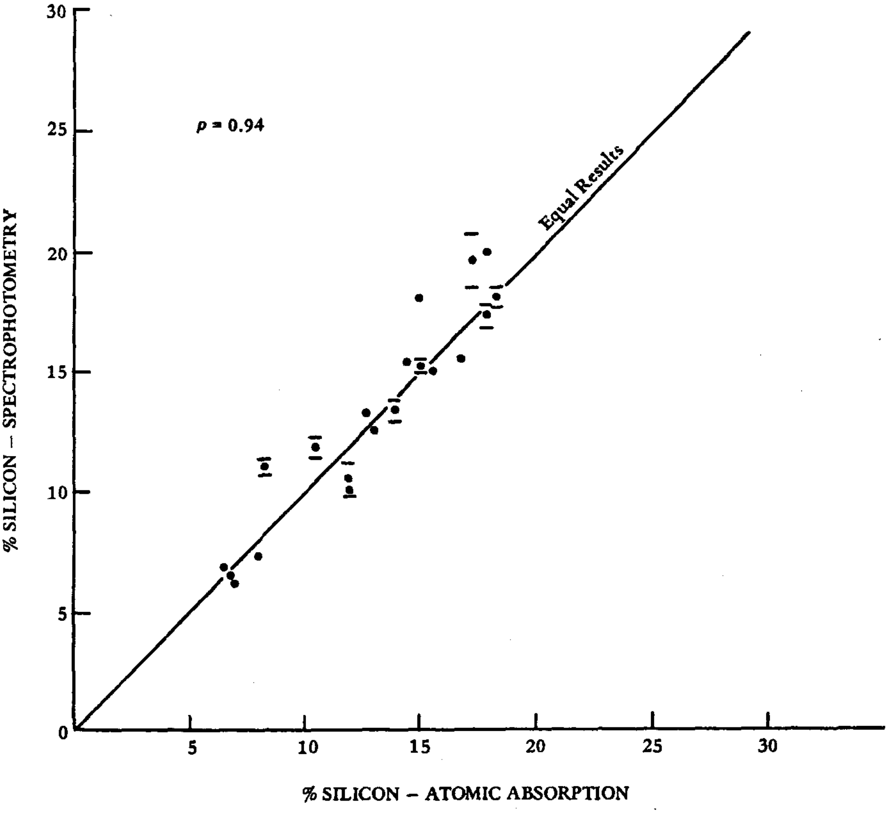

FIGURE 2 Silicon analysis of particulate matter samples by spectrophotometry and atomic absorption.

Results with NBS standard reference materials support these conclusions. The emission technique displayed relatively poor accuracy and precision. The AA method indicated equivalency, if not an improvement in accuracy relative to the reference method.

The differences in results between the AA and reference methods reflect in part, the use of lithium metaborate for the AA method instead of the

TABLE II

Precision and accuracy of silicon analysis of NBS standard reference materials by spectrophotometric, emission spectrographic and atomic absorption techniques

Substance		Spectrophotometry[a]				Emission				Atomic Absorption			
SRM	% Si	Mean ($n = 8$)	Stnd. Dev.	% Coeff. of Var.	Accuracy[c] % error	Mean ($n = 8$)	Stnd. Dev.	% Coeff. of Var.	Accuracy % error	Mean ($n = 8$)	Stnd. Dev.	% Coeff. of Var.	Accuracy % error
99a	30.5	21.9	1.37	6.2	−27.9	19.2	4.0	20.7	−37	28.6	0.85	3.0	−6.2
99a[b]	30.5	25.8	1.54	5.9	−15.4								
97a	20.4	19.5	0.54	2.7	− 4.4	15.6	3.3	21.4	−24	18.3	1.4	7.4	−10.3
1013	11.3	8.60	0.23	2.7	−23.9	7.13	1.4	19.8	−37	8.44	0.29	3.5	−25.3
1013[b]	11.3	10.6	0.68	6.4	− 6.2								
1015	9.65	9.32	0.84	9.1	− 3.4	8.00	2.1	12.5	−17	9.96	0.27	2.7	+3.3
103a	2.16	1.98	0.10	5.2	− 8.3	2.33	1.1	47.3	+ 7.9	2.14	0.42	19.5	−0.9
104	1.19	1.04	0.12	11.4	−12.6	0.75	0.12	16.0	−37	1.20	0.20	16.3	+1.7
Overall:	12.5	10.4	0.65		−17	8.8	2.4		−30	11.4	0.70		−9

[a] With sodium carbonate fusion except as noted.

[b] With lithium metaborate fusion, not included in the "overall" values shown.

[c] Accuracy, % error = $\frac{(\text{Mean} - \text{NBS reported values}) \times 100}{\text{NBS reported values}}$.

Na_2CO_3 used for the reference procedure. Observations during fusion of atmospheric samples in Na_2CO_3 indicate such samples to be substantially easier to fuse than the NBS standards. Thus, with such samples, it is highly probable that lithium metaborate and Na_2CO_3 would give equivalent results. However, where more refractory compounds are involved lithium metaborate appears to offer substantial advantage. Nevertheless, for routine analysis of atmospheric samples the lower cost of Na_2CO_3 commends its use.

Based on the present findings the AA method with lithium metaborate fusions has been tentatively adopted as an equivalent, alternative method for silicon analysis in atmospheric particulate matter as well as other samples.

Ackowledgements

We wish to thank Nancy Yang and Mr. Arthur Alcocer of AIHL for assistance in this work and Mr. Arnold Koch of Perkin-Elmer for providing instrumentation and assistance.

References

1. K. Rahn, J. J. Wesolowski, W. John and H. R. Ralston, *JAPCA* **21,** 403 (1971).
2. I. H. Blifford and D. A. Gillette, *Atmos Environ.* **6**(7), 463 (1972).
3. L. Shapiro and W. Brannoch, Rapid analysis of silicate rocks. Geological Survey Bulletin No. 1036–C, Department of the Interior. Revised from Circular 165 (1956).
4. C. O. Ingamells, *Anal Chem.* **52,** 323 (1970).
5. N. H. Suhr and C. O. Ingamells, *Anal. Chem.* **38,** 730 (1966).
6. J. H. Medlin, N. H. Suhr, and J. B. Bodkin, *Atomic Absorption Newsletter* **8,** 25 (1969).
7. J. W. Yule and G. A. Swanson, *Atomic Absorption Newsletter* **8,** 30 (1969).
8. P. L. Boar and L. K. Ingram, *Analyst* **95,** 125 (1970).
9. Analytical methods for atomic absorption spectrophotometry. Perkin-Elmer Corporation, Norwalk, Conn., March, 1971.
10. W. Bunting, *Anal. Chem.* **16,** 612 (1944).
11. J. L. Seeley *et al.*, *Applied Spectroscopy* **26,** 456 (1972).
12. M. S. Miller, S. K. Friedlander, and G. M. Hidy, *J. Coll. Interface Sci.* **39** (1), 165 (1972).