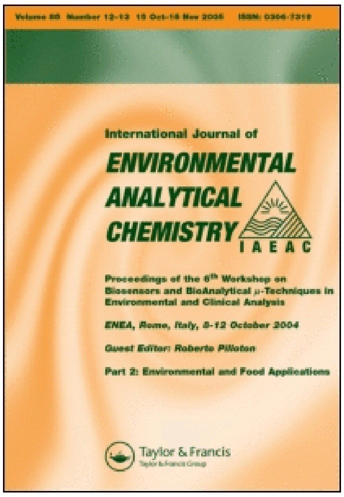

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Sulphur Determination in Coal by Proton Activation Analysis

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The technique of charged particle activation analysis has been employed to precisely and speedily determine sulphur concentration in NBS coal 1632a. Coal samples and sulphur standards were pellitized and then activated with 10.3 MeV protons to produce the $^{34}S(p, n)^{34m}Cl$ reaction. Typically, reproducibility experiments were of the order of 2%, while detection limits of 1500 ppm (0.15% by weight) of sulphur could be attained.

1. INTRODUCTION

Major concern about the environmental and toxicological effects of fossil-fuel burning has led to the increased use of various multi-elemental methods in coal analysis. At present there are several nuclear analytical techniques being employed to determine major,

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minor and trace constituents in coal. These include neutron activation, neutron capture prompt gamma-ray and photon activation analysis,[1-5] proton-induced X-ray emission,[6] proton-induced gamma-ray analysis,[7] and X-ray fluorescence.[8] Surprisingly, charged particle activation analysis (CPAA), while used successfully in various metallurgical, archaeological and solid-state studies[9-13] (and many more), has received little attention with respect to environmental samples.[14-16] Other than our own present study it appears that CPAA has only been used for analysis of oxygen content[17,18] in coal and for sulphur determination in crude oils and petroleum products.[19,20]

Because of the particular interest of sulphur concentrations in coal and the major contribution of sulphur to acid rain and snow, the National Bureau of Standards (NBS) in Washington has recently updated its standard certification of trace elements in coal (SRM 1632a) including a new certified value for sulphur. We wish to report on the determination of sulphur in NBS coal 1632a by CPAA in a reliable and non-destructive fashion. It is hoped that future routine sulphur analysis of various coal samples can use this new certified sulphur concentration as a standard along with charged particle activation analysis.

2. EXPERIMENTAL

2.1 Sample preparation

Samples of NBS coal 1632a and of high-grade sulphur (used as standards) were pelletized under a pressure of 5 tons per cm^2. The weight of the samples was pre-determined to be thick enough to stop the incoming proton beam. Typical thicknesses were of the order of 3 mm for both samples and standards. Each coal sample and sulphur standard was then individually wrapped in a 100 μm high-purity aluminum foil with a 25 μm iron foil placed in front. The iron foil acted as a flux monitor while the aluminum foil prevented any recoil Co atoms from contaminating the samples or standards.

2.2 Irradiation and counting

Irradiations were performed with the CNRS variable energy cyclotron at Orléans. All samples were activated in air by 12 MeV protons passing from vacuum through a 25 μm titanium foil into air. The proton energy at the surface of the samples was calculated to be 10.33 MeV. A complete experimental set-up is depicted in Figure 1. Sulphur standards were irradiated for a period of 2 min at 10 nA while coal samples were activated for 15 min at 500 nA. One of the main problems of proton activation of coal is the high abundance of carbon which undergoes the following prominent nuclear reaction:

$$^{13}C(p,n)^{13}N \qquad t_{1/2}=9.97\ \text{m}.$$

It is therefore necessary to wait about 2 hours until the high amount of radioactivity produced from the β^+ of ^{13}N has substantially decayed away. The three gamma-rays which can be detected from the decay of ^{34m}Cl have energies of 146.4 keV, 1176.1 keV and 2127.4 keV. However, for quantitative results, only the 146.4 keV gamma-ray is of use. The reasons for this are two-fold: (a) the 146.4 keV gamma-ray accounts for 53% of all the disintegrations of $34^{m}Cl$, and (b) the detection efficiency for a Ge(Li) detector of a gamma-ray of this energy is about at the maximum. It has been previously shown that the experimental number of gamma/min for the 146.4 keV gamma-ray was more than 30 times than that of the 1176.1 keV gamma-ray.[21] The 2127.4 keV gamma-ray is also of no practical use since the efficiency of a Ge(Li) detector at this energy is very low.

A Ge(Li) detector having a resolution of 2.2 keV at full width half-maximum for 1.33 MeV photons and a measured efficiency of 11.4% was used for all the measurements. Spectra were accumulated with a Tracor Northern 1750 analyser. Deadtimes were always kept below 10%. Peak areas were simply calculated by taking an average background on either side of the 146.4 keV gamma-ray peak and subtracting the background area from the total area of the peak. A typical partial spectrum can be seen in Figure 2. Considering the proximity of the 141.2 keV peak, arising from the $^{90}Zr(p,n)^{90}Nb$ reaction, the importance of a Ge(Li) detector possessing very good resolution is clearly evident.

For quantitation, the method of the average cross-section was used.[22] The concentration x of an element is given by the following

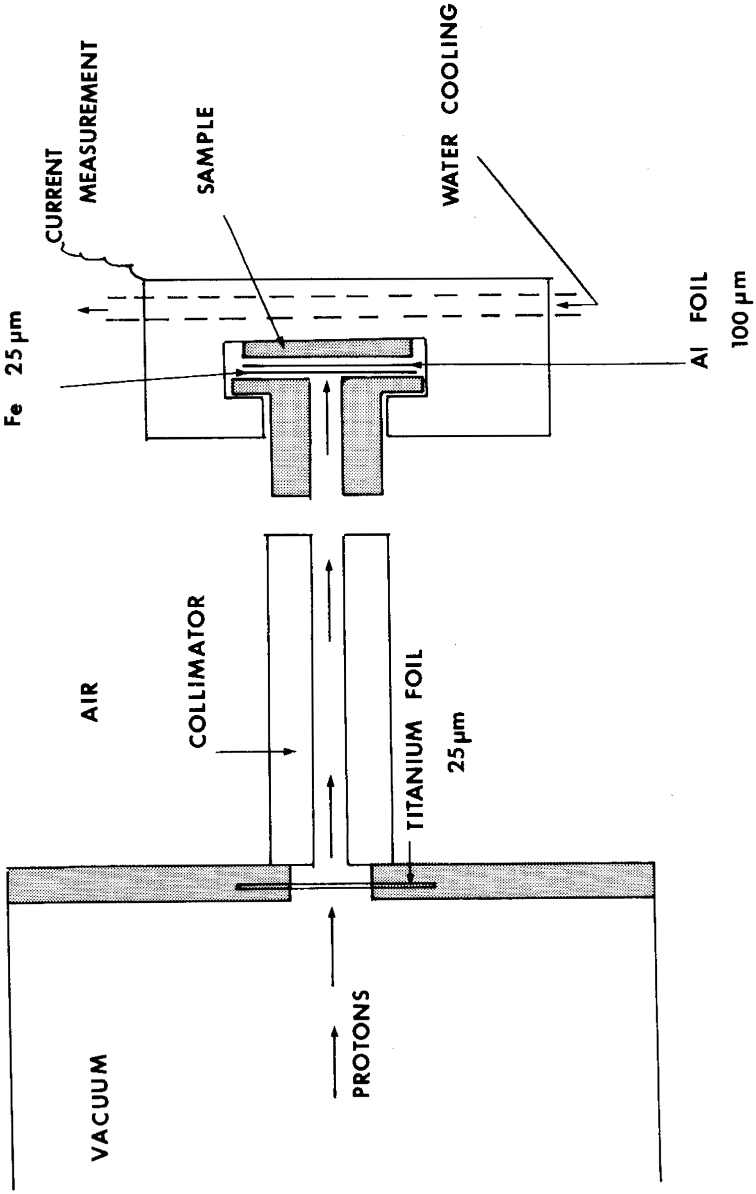

FIGURE 1 Proton activation analysis set-up.

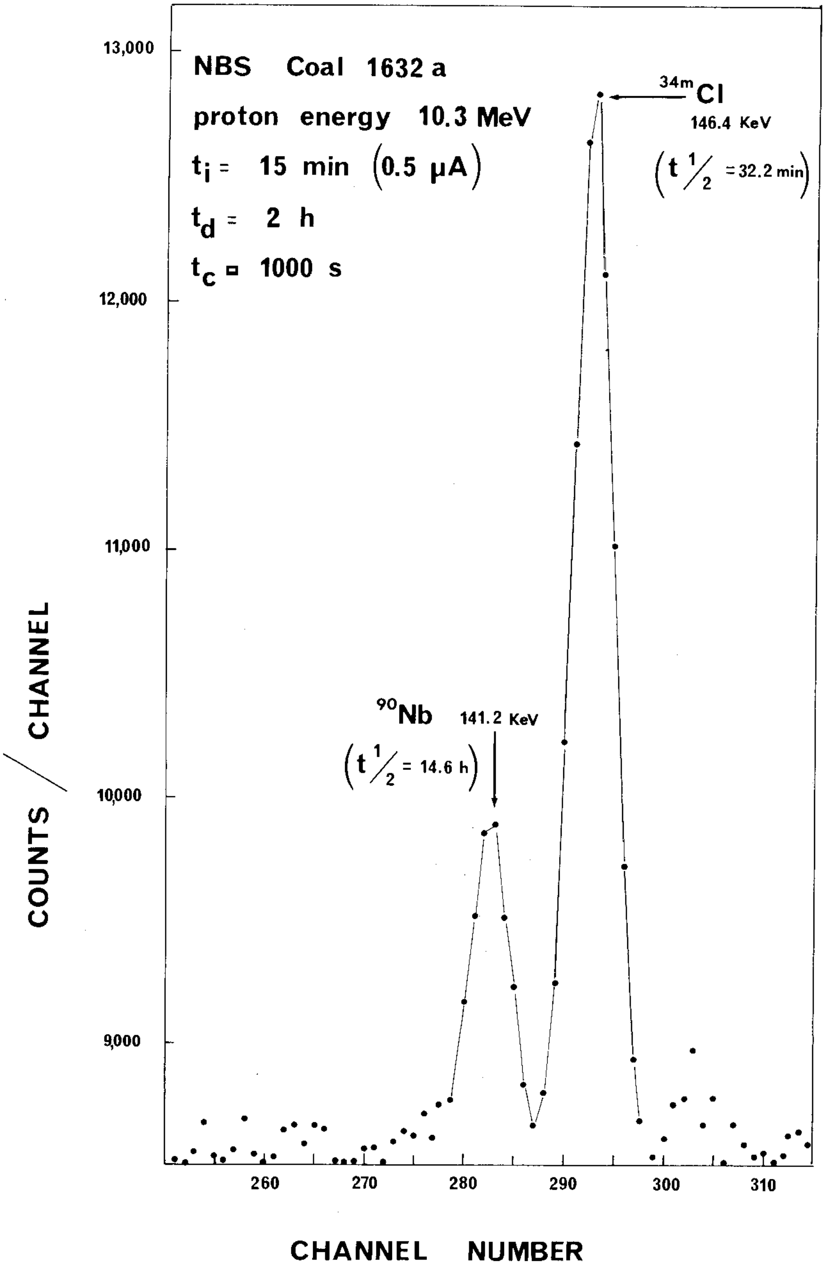

FIGURE 2 A typical partial proton activation analysis spectrum for NBS coal 1632a.

formula:

$$x_{\text{ppm}} = 10^6 \times \%\ \underset{\text{in the standard}}{\text{fraction element of interest}} \cdot \frac{A_x}{A_{\text{st}}} \cdot \frac{R_{\text{st}}}{R_x} \cdot \frac{F_{\text{st}}}{F_x}$$

where A_x and A_{st} are the activities of sample and standard respectively; R_x and R_{st} are the ranges of the incident particles in the sample and in the standard, respectively; and F_x and F_{st} are the activities of the Fe flux monitors for the sample and standard respectively. For samples which were not measured under the same conditions (irradiation, decay and counting periods) the specific activities were multiplied by the appropriate correction factors. Stopping powers were calculated from published data.[23] For coal a calculation was based on the major elemental composition of NBS 1632a.[24] These included H(3.7%), C(63%), N(1.27%), Mg(0.13%), Al(2.94%), Si(5.8%), S(1.62%), K(0.42%), Ca(0.23%), Ti(0.16%) and Fe(1.11%). The rest was assumed to be oxygen. Such an assumption is well-justified since the remaining trace elements are in parts per million or parts per billion concentrations. It should be strongly pointed out that if NBS coal 1632a was to be used as a standard to determine sulphur or other trace elements of interest in other coals the need for the calculation of ranges or stopping powers would probably not be necessary since the matrix composition of major elements in various coals is similar.

The use of an Fe flux monitor has been shown to be well-justified and reliable.[21] In experimental practice the activity of the 846.7 keV gamma-ray ($t_{1/2} = 78.5d$) from the $^{56}\text{Fe}(p, n)^{56}\text{Co}$ reaction is used.

Gamma-ray attenuation coefficients were calculated for the 146.4 keV gamma-ray from published tables[25] both for the sulphur standard and for NBS 1632a. As for the ranges or the stopping powers, the calculation of the gamma-ray attenuation coefficients for coal was based on the major elemental composition. It was found that the effect was small (of the order of 2%) for both coal sample and sulphur standard and that their computed difference could be considered to be negligible.

3. RESULTS AND DISCUSSION

The experimental results for the sulphur concentration in NBS coal

1632a (along with values from other studies) are shown in Table I. Five determinations of the coal samples and sulphur standards were done to achieve a good precision. The detection limits of 0.15% (as determined by Currie's criterion[26]) by sulphur weight appear to be adequate for typical sulphur concentrations found in coal. As usual in nuclear analytical methods the reproducibility of the results is the most statistically significant criterion. Results obtained for the five values gave a precision of 2% and an accuracy of 2% when compared to the NBS certified value of 1.62%±0.03.

TABLE I

Concentration of sulphur in NBS coal 1632a

This work	NBS value	Other work		
1.59%±0.03	1.62%±0.03	1.59%±0.02[a] 1.5% ±0.7[d]	1.45%±0.23[b]	1.58%±0.06[c]

[a] Reference 3 neutron-capture prompt gamma-ray analysis.

[b] Reference 27 neutron activation analysis and X-ray fluorescence.

[c] Reference 28 neutron-capture prompt gamma-ray analysis.

[d] Reference 29 neutron activation analysis.

The other values for sulphur concentrations are shown for comparison. The compiled work by Gladney[27] shows a value of 1.45%±0.23 based upon three determinations (two by activation analysis and one by X-ray fluorescence). This value (based mainly on neutron capture prompt gamma-ray analysis) has now been updated[28] to 1.58%±0.06 and will be published soon. Special mention should be given to the work of Failey *et al.*[3] Their reported value of 1.59%±0.02 also done by prompt gamma activation analysis is in excellent agreement with this present work and others. Their reported detection limit for sulphur is 180 ppm which indeed is excellent. However, a very long bombarding time of 20 hours was necessary to achieve this. A detection limit of 1% of sulphur by weight in coal is also reported by Macias and Barker using proton-induced gamma-ray analysis.[7] Our present work has achieved a detection limit of about a factor seven times lower.

It would appear that the published nuclear analytical methods used to determine sulphur are all in excellent agreement with each other and only slightly lower than the reported NBS value.

In conclusion we feel that proton activation analysis can serve as a very useful, reliable and non-destructive analytical tool to determine sulphur concentrations in coal. Furthermore many samples can be analyzed in a single working day making this technique desirable in any routine environmental program. It is hoped that further experiments of this sort may soon be undertaken not only for sulphur analysis in coal but also for other elements in various environmental samples.

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Note added in proof: A recent paper[30] has shown that large inaccuracies (upwards to ±29%) in neutron activation analysis may be a result from isotopic differences in sulphur standards and samples. Inaccuracies may also be inherent in proton activation analysis upwards to ±15%. However if the isotopic composition of the standard is known the error may be reduced to ±7%. To that end exact isotopic sulphur composition of NBS 1632a coal and other NBS coal samples are presently being investigated.

A very new sulphur value of 1.59% has just been certified by NBS.[31]

References

1. R. E. Jervis, R. Ho and B. Tiefenbach, *J. Radioanal. Chem.* **71,** 225 (1982).
2. J. H. Klie and H. D. Sharma, *J. Radioanal. Chem.* **71,** 299 (1982).
3. M. P. Failey, D. L. Anderson, W. H. Zoller and G. E. Gordon, *Anal. Chem.* **51,** 2209 (1979).
4. V. Galatanu and Ch. Engelmann, *J. Radioanal. Chem.* **67,** 143 (1981).
5. K. W. D. Ledingham, M. G. Kelliher and S. D. Robertson, *J. Radioanal. Chem.* **71,** 169 (1982).
6. W. D. Ehman, "Applications of INAA and PIXE to the analysis of coal", in: *Third International Conference on Nuclear Methods in Environmental and Energy Research,* Columbia, Missouri, U.S.A. October 10–13, 1977, pp. 284–293.
7. E. S. Mascias and J. H. Barker, *J. Radioanal. Chem.* **45,** 387 (1978).
8. J. W. Prather, J. A. Guin and A. R. Tarrer, "X-ray fluorescence analysis of trace elements in coal and solvent refined coal", in *Analytical Methods for Coal and Coal Products,* Vol. III, chapter 49, Academic Press, 1979.
9. G. Blondiaux, A. Giovagnoli, M. Valladon and J. L. Debrun, *IEEE Transactions on Nuclear Science,* Vol. NS-30, 1619 (1983).
10. G. Blondiaux, M. Valladon, J. L. Debrun, P. Benaben, M. Bouchacourt, C. Brodhag and F. Thevenot, *J. Less-Common Metals* **82,** 105 (1981).
11. J. N. Barrandon, *J. Radioanal. Chem.* **55,** 765 (1981).

12. P. Debefve, H. P. Do, C. Friedli, P. Lerch and W. Renaud, *Radiochem. Radioanal. Lett.* **40,** 389 (1979).
13. M. Vallandon, G. Blondiaux, C. Koemmever, J. Hallus, G. Poiblaud, A. Haber and J. L. Debrun, *J. Radioanal. Chem.* **58,** 165 (1980).
14. L. Zikovsky and E. A. Schweikert, *J. Radioanal. Chem.* **37,** 571 (1977).
15. T. Al-Naimi, M. I. Edwards and J. H. Fremlin, *Phys. in Med. and Biol.* **25,** 719 (1980).
16. M. S. Clemson, "The determination of low-Z elements in atmospheric aerosols by charged particle induced nuclear reaction", Thesis, University of California, Berkeley, U.S.A., 1979.
17. D. J. Schyler and A. P. Wolf, "A study of coal oxidation by charged particle activation analysis", in *Fourth International Conference on Nuclear Methods in Environmental and Energy Research,* Columbia, Missouri, U.S.A., April 14–17, 1980, pp. 612–620.
18. D. J. Schyler, T. J. Ruth and A. P. Wolf, *Fuel* **58,** 208 (1979).
19. J.-P. Thomas and E. A. Schweikert, *Nucl. Instrum. and Meth.* **99,** 461 (1972).
20. T. D. Burton, O. L. Swindle and E. A. Schweikert, *Radiochem. Radioanal. Lett.* **13,** 191 (1973).
21. J. L. Debrun, J. N. Barrandon and P. Benaben, *Anal. Chem.* **48,** 167 (1975).
22. E. Ricci and R. L. Hahn, *Anal. Chem.* **39,** 794 (1967).
23. J. F. Ziegler, *H Stopping Powers and Ranges in All Elements* (Pergamon Press, Oxford, 1977).
24. M. S. Germani, I. Gokmen, A. C. Sieglo, G. S. Kowalczyk, I. Olmez, A. M. Small, A. L. Anderson, P. P. Failey, M. C. Gulovali, C. E. Choquette, E. A. Lepel, G. E. Gordon and W. H. Zoller, *Anal. Chem.* **52** 240 (1980).
25. C. M. Davisson, "Interaction of γ-radiation with matter", *Alpha-, Beta- and Gamma-Ray Spectroscopy* (K. Siegbahn, ed.), Vol. I, chapter II, North-Holland, 1979.
26. L. A. Currie, *Anal. Chem.* **40,** 586 (1968).
27. E. S. Gladney, *Anal. Chem. Acta.* **118,** 385 (1980).
28. E. S. Gladney, Private communication, Los Alamos Scientific Laboratory, New Mexico.
29. R. Ho, M.Sc. Thesis, University of Toronto, 1981.
30. R. F. Fleming and R. M. Lindstrom, *Trans. Am. Nucl. Soc.* **41,** 223 (1982).
31. R. F. Fleming, Private communication, National Bureau of Standards (NBS), Washington.