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A RAPID METHOD FOR ASSAYING SULFUR USING PROTON ACTIVATION ANALYSIS*

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A novel application of charged particle activation analysis is presented involving short irradiations of 1 sec coupled with the measurement of very short-lived nuclides. The case studied deals with the determination of sulfur using $^{32}\text{S}(p,n)^{32}\text{Cl}$. This activation reaction features a high abundance target isotope and a product nuclide of very short half-life (300 msec) emitting high energy positrons. Counting was performed with a Cherenkov

detector at the irradiation site immediately after bombardment. The experimental approach for optimizing the counting conditions is described and the activation curve for $^{32}\text{S}(p,n)^{32}\text{Cl}$ is given for proton energies up to 22.5 MeV. The sensitivity based on experimental data is estimated at $\approx 50 \mu\text{g}/\text{cm}^2$. The application of this technique to petroleum products with sulfur contents ranging from 3.18% to 0.72% is discussed.

1. Introduction

Charged particle activation analysis has been based so far on the measurement of radioisotopes with half-lives ranging in most cases from minutes up to several days. No work has been reported on the analytical exploitation of nuclear reactions yielding radioactive species with half-lives of fractions of seconds. Such an approach offers, however, several advantages by providing for rapid and sensitive methods of analysis in maximizing the buildup of the radioisotope of interest close to saturation levels and in permitting the use of high beam intensities even for target materials of low heat resistance. The case studied deals with the determination of S using $^{32}\text{S}(p,n)^{32}\text{Cl}$. This activation reaction features: (a) a target isotope of high abundance (95%); (b) a product nuclide of very short half-life (300 msec) and emitting high energy positrons ($E_{\beta^+ \text{max}} = 9.9 \text{ MeV}$). The half-life of ^{32}Cl makes a sample transfer impractical, accordingly counting must be performed immediately after the bombardment at the irradiation site. From the standpoint of an analytical application the selectivity and sensitivity attainable will thus largely depend upon the performance of a detector operating in a radiation background due to a host of radioisotopes in the target and the surrounding materials. Among the different types of possibly useful detectors for measuring the β^+ -emission of ^{32}Cl , a Cherenkov counter appeared as a practical solution, permitting some, although by no means total, selectivity for positrons and their respective

energies and requiring only simple counting electronics.

The basic concept of a Cherenkov counter and its application to radioisotope counting have been discussed by Belcher¹⁾ and Ross²⁾. These authors have discussed the detection of relatively long lived ($T_{1/2} \geq 1 \text{ h}$) β^- emitters, especially as a complement to liquid scintillation counting. Lukens³⁾ has used Cherenkov counting for detecting the short-lived ^{16}N ($T_{1/2} = 7.35 \text{ sec}$) in an oxygen analysis method based on $^{16}\text{O}(n,p)^{16}\text{N}$.

In the present work the following questions are successively examined: study of the reaction $^{32}\text{S}(p,n)^{32}\text{Cl}$ and the use of a Cherenkov detector for measuring ^{32}Cl , quantitative importance of possibly interfering nuclear reactions, experimental sensitivity estimate and application of this analytical technique to the determination of sulfur in petroleum products.

2. Experimental

2.1. PREPARATION OF TARGETS

Thin sulfur targets were prepared by evaporating S in vacuum onto aluminum backings ($6.75 \text{ mg}/\text{cm}^2$). The thickness of the sulfur deposits was determined by weighing and was in the order of $1-2 \text{ mg}/\text{cm}^2$. Pelletized powders (S, Ca, Cr) or solid discs (Si, Fe, Ti) were used for the thick target irradiations. For the petroleum products lucite sample containers holding approximately 3 cm^3 and sealed with an aluminum window of $12.5 \mu\text{m}$ thickness were used.

2.2. IRRADIATION

Irradiations were carried out using 22.5 MeV protons delivered by the 88" sector-focused variable energy cyclotron at Texas A&M University. Beam focusing onto the target was performed visually using a phos-

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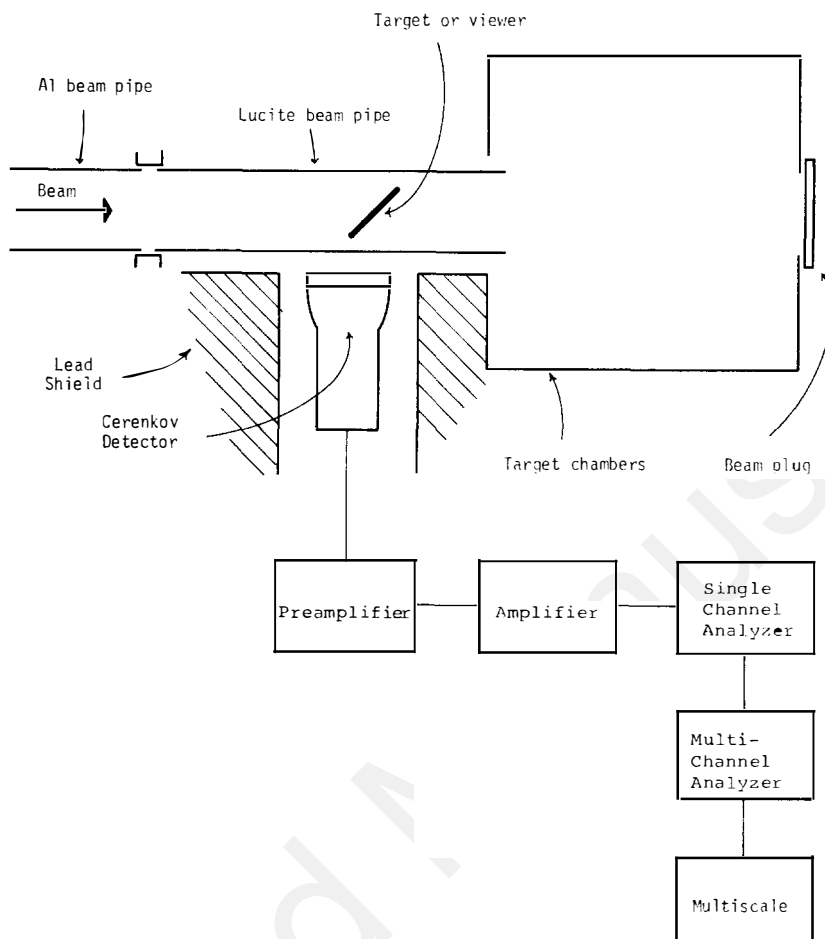


Fig. 1. Experimental set-up.

phorescent viewer monitored with a closed circuit TV system. In the case of thin target bombardments the beam was stopped with a thick Ta plate approximately 50 cm behind the target detector site. The irradiation setup and associated counting electronics are given in fig. 1. The irradiation times usually of 1 sec were determined by the opening and closing of a Faraday cup, which also served for monitoring the beam intensities before and after the 1 sec irradiations. Great care was taken to reduce as much as possible the radiation level at the target-detector site, by carefully focusing the beam onto the target, by shielding of the Cerenkov detector, and by utilizing for the beam control a Faraday cup located in the machine vault separated from the irradiation site by a heavily shielded wall.

For the work with the petroleum samples a modified setup was used. The irradiation was carried out in air, with the detector placed in the beam axis immediately behind the container.

The irradiation-counting sequence was controlled automatically with a timer thus providing for the reproducibility needed to carry out on the same sample repetitive irradiations and accumulation of the decay data for achieving better counting statistics.

2.3. CHERENKOV DETECTOR

A detailed discussion on the Cherenkov effect induced by relativistic charged particles passing through a transparent dielectric medium has been given by Jelley⁴). The main criterion for selecting a converter material was to achieve maximum efficiency, this led to the adoption of a non-focalizing detector and a converter material with radiation yield higher than that of water or lucite converters. The plastic material used ("Pilot 425" available from New England Nuclear Corp., Pilot Chemicals Division, Watertown, Mass.) offers increased efficiency due to the presence of a wavelength shifter providing for re-emission at 450 nm which corresponds to the optimum wavelength for the

TABLE 1
Proton induced reactions on sulfur.

Isotopic abundance	Reaction	Threshold	Half-life	β^+ emission	γ emission
95%	$^{32}\text{S}(p,n)^{32}\text{Cl}$	14.4 MeV	0.28-0.32 sec	9.9 MeV	0.511 MeV 200% 2.24 MeV 70% 4.77 MeV 14% 4.29 MeV 7%
95%	$^{32}\text{S}(p,d)^{31}\text{S}$	13.27 MeV	2.6-2.7 sec	4.42 MeV	0.511 MeV 200% 1.27 MeV 1.1%
95%	$^{32}\text{S}(p,\alpha)^{29}\text{P}$	4.07 MeV	4.2-4.6 sec	3.95 MeV	0.511 MeV 200% 1.29 MeV 0.8% 2.43 MeV 0.2%
4.22%	$^{34}\text{S}(p,n)^{34}\text{Cl}$	6.45 MeV	1.56 sec	4.46 MeV	0.511 MeV 200%
0.76%	$^{33}\text{S}(p,n)^{32}\text{Cl}$	6.55 MeV	2.4-2.9 sec	4.55 MeV	0.511 MeV 200% 2.9 MeV 0.2%

photomultiplier tube. The characteristics of "Pilot 425" are as follows: specific gravity of 1.19 and index of refraction of 1.49⁵). The 3" x 3" detector photomultiplier assembly was tested with ^{24}Na , ^{32}P and ^{90}Y emitting β^- particles with maximal energies of 1.39, 1.71, and 2.28 MeV respectively.

3. Results and discussion

3.1. PROTON INDUCED REACTIONS OF SULFUR

Table 1 lists the different nuclear reactions possible with 22.5 MeV protons on sulfur. As already mentioned, the reaction selected, $^{32}\text{S}(p,n)^{32}\text{Cl}$, involves the target nuclide of highest isotopic abundance and yields a product isotope emitting positrons of a distinctive maximal energy ($E_{\beta^+ \text{max}} = 9.9$ MeV).

3.2. IDENTIFICATION OF ^{32}Cl

The analytical exploitation of very short lived species requires a selective detection based on the type and energy of radiation emitted and the half-life. In the specific case of positron counting with a Cherenkov detector a compromise has to be found between the selectivity and the detection efficiency.

TABLE 2
Effect of threshold setting on the relative activities of ^{32}Cl and ^{29}P .

Threshold channel	Relative activity at t_0		Ratio $A_{t_0}^{32}\text{Cl}/A_{t_0}^{29}\text{P}$
	^{32}Cl	^{29}P	
20	35,000	800	44
40	15,000	180	83
60	10,000	≈ 30	≈ 340
80	4,200	< 10	> 420

The optimum operating conditions for the detector and the counting electronics must be determined experimentally for each type of sample. The procedure used can be illustrated first with a non-optimized set of data shown in fig. 2. The counting sequence was started prior to the start of the irradiation. The data

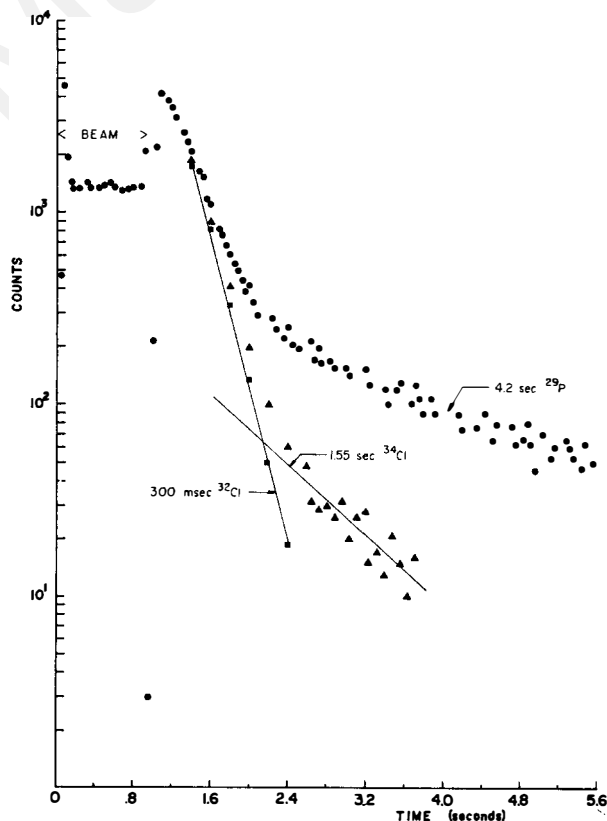


Fig. 2. Decay curve from a thick sulfur pellet with a low threshold setting on the Cherenkov detector.

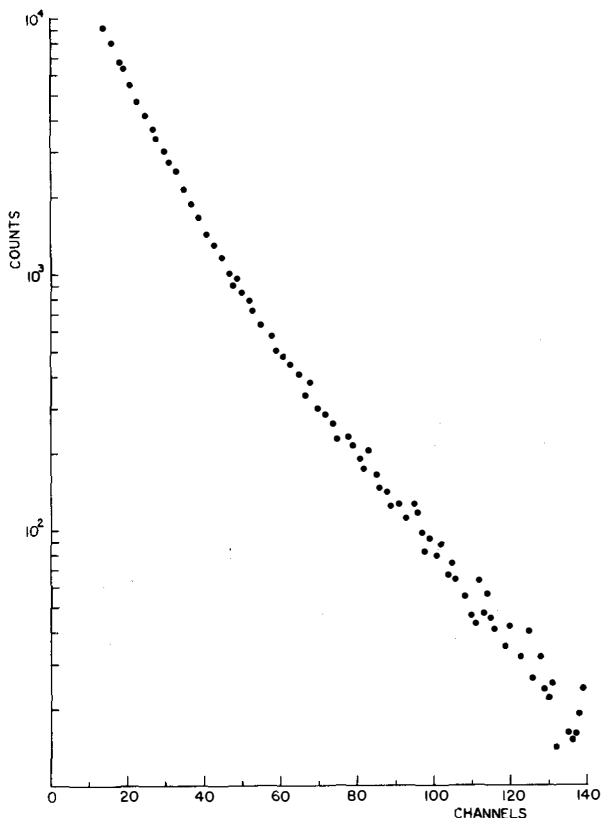


Fig. 3. Cherenkov spectrum from a thick sulfur pellet.

recorded differs from an activation and decay curve in two important aspects: (a) no buildup curve is apparent; this is due to the fact that as soon as the beam is bombarding the target the detector becomes saturated; (b) at the end of irradiation, the detector is overloaded for a very short time before recovering and providing the expected decay data. This irradiation and decay data was obtained on a thick sulfur target with a low energy threshold setting and an aluminum absorber in front of the Cherenkov counter thick enough to stop β particles with $E < 3$ MeV. A zero energy threshold setting and use of absorbers alone resulted in such an overload of activity on the counting system that no short half-lives could be detected. In fact, the use of absorbers is only of value in cases where screening out of interfering low energy β activity is needed to reduce the overall countrate to be processed. The decay curve in fig. 2 consists of three components, a 300 msec half-life assigned to ^{32}Cl , a 1.55 sec half-life tentatively assigned to ^{34}Cl and a 4.2 sec half-life assigned to ^{29}P . It is clear that for a successful detection of ^{32}Cl the ratio of the activities due to ^{32}Cl and ^{29}P must be maximized. This can be achieved by setting the energy threshold considering the β^+ energies of the two main

species involved: ^{29}P ($E_{\beta^+ \text{max}} = 3.95$ MeV) and ^{32}Cl ($E_{\beta^+ \text{max}} = 9$ MeV). The activities for these species and their respective ratios as a function of threshold settings and for constant irradiation conditions are given in table 2. To illustrate the discrimination levels used, a typical Cherenkov spectrum obtained after irradiation of a thick sulfur target is presented in fig. 3. The effectiveness of the experimental procedure for optimizing the counting conditions is illustrated in fig. 4, showing a pure ^{32}Cl decay curve obtained from a thick sulfur target using no absorber but a high threshold energy setting.

3.3. ACTIVATION CURVE

The reaction $^{32}\text{S}(p,n)^{32}\text{Cl}$ was studied for proton energies up to 22.5 MeV. While the integrated activation curve presented in fig. 5 indicates the desirability of possibly using protons of energies higher than 22.5 MeV, this latter energy must in practice be considered an upper limit, in order to avoid production of ^8Li ($T_{1/2}$: 800 msec, $E_{\beta^+ \text{max}}$: 13 MeV) which becomes possible for a number of matrix elements with $E_p > 22.5$ MeV. The integrated activation curve was obtained using a

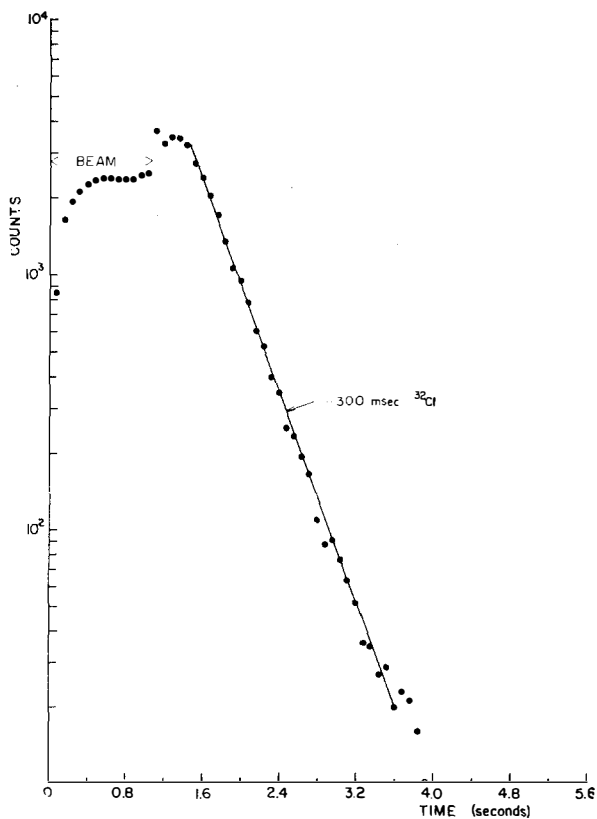


Fig. 4. Decay curve from a thick sulfur pellet with a high threshold setting on the Cherenkov detector.

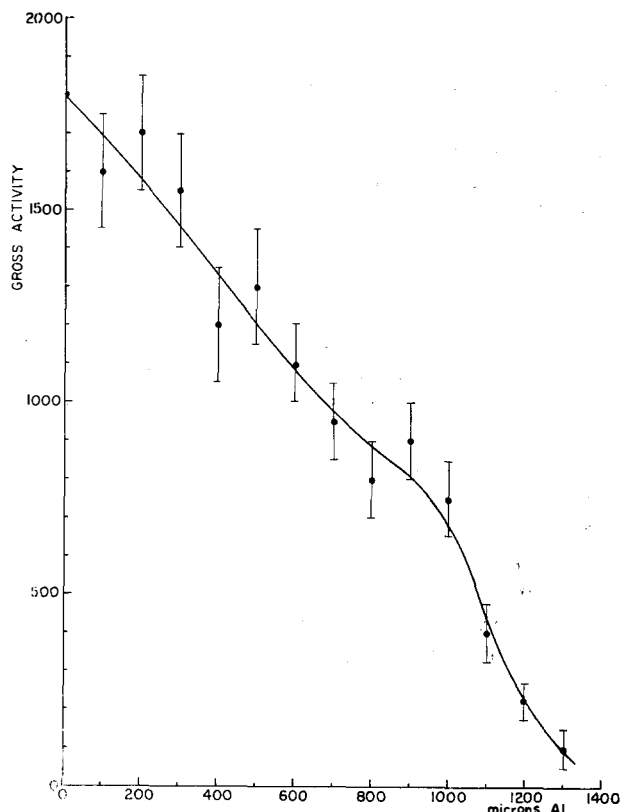


Fig. 5. Activation curve for the reaction $^{32}\text{S}(p,n)^{32}\text{Cl}$.

thick sulfur target with aluminum absorbers of varying thicknesses in front. Considering the relative amounts of sulfur and aluminum present possible interferences due to aluminum were negligible.

3.4. INTERFERING REACTIONS

Several nuclear reactions yielding radioisotopes emitting high energy positrons with half-lives close to that of ^{32}Cl were evaluated. Their characteristics and relative activities compared to $^{32}\text{S}(p,n)^{32}\text{Cl}$ are given

TABLE 3
Characteristics of $^{32}\text{S}(p,n)^{32}\text{Cl}$ compared to those of interfering reactions.

Reaction	Half-life	Threshold	Emission		Relative Cherenkov counts at t_0
			β^+	γ	
$^{32}\text{S}(p,n)^{32}\text{Cl}$	0.360 sec	14.3 MeV	9.9 MeV	0.511, 2.24, 4.77, 4.29 MeV	$2000 \pm 10\%$
$^{28}\text{Si}(p,n)^{28}\text{P}$	0.280 sec	15.6 MeV	11.8 MeV	0.511, 1.78, 2.6-7.6 MeV	$4600 \pm 10\%$
$^{40}\text{Ca}(p,n)^{40}\text{Sc}$	0.180 sec	15.9 MeV	9.2 MeV	0.511, 3.73, 0.73 MeV	$460 \pm 15\%$
$^{54}\text{Fe}(p,n)^{54}\text{Co}$	0.190 sec	10.3 MeV	7.23 MeV	0.511 MeV	≤ 60
$^{46}\text{Ti}(p,n)^{46}\text{V}$	0.420 sec	9.6 MeV	6.05 MeV	0.511 MeV	< 10
$^{50}\text{Cr}(p,n)^{50}\text{Mn}$	0.290 sec	10.0 MeV	6.6 MeV	0.511 MeV	< 10

in table 3. The only sizable interference is due to silicon, requiring for an essentially interference-free sulfur determination that the concentration level of silicon with respect to that of sulfur be $< 1:10$.

3.5. SENSITIVITY ESTIMATE

To assess the sensitivity of this method sulfur was determined in presence of aluminum, the targets consisting of thin sulfur films ($\approx 1 \text{ mg/cm}^2$) deposited onto aluminum foils (6.75 mg/cm^2). Different reactions can occur on aluminum yielding short lived radioisotopes, all β^+ -emitters (table 4). The main activity induced by 22.5 MeV protons on aluminum is that due to $^{27}\text{Al}(p,d)^{26}\text{Al}^m$. Aluminum constitutes thus a typical, practical case where sulfur is sought in presence of abundant β^+ and γ -ray matrix activity. Beam intensities of up to $5 \mu\text{A}$ were used requiring consequently an upward adjustment of the energy threshold in order to minimize the contribution due to $^{26}\text{Al}^m$. This is illustrated in fig. 6 with two decay curves obtained with a 1 sec $5 \mu\text{A}$ irradiation and a threshold setting in channel 160, (a) for a thin sulfur deposit on an aluminum foil where the ^{32}Cl decay is readily apparent and (b) an aluminum foil alone showing that contributions due to $^{26}\text{Al}^m$ have been eliminated. This data can serve as an example for estimating a detection limit. Assuming a minimum of 30 counts/125 msec for ^{32}Cl at the end of irradiation (approximately equivalent to the aluminum activity), the minimum amount of sulfur detectable on an aluminum foil of 6.75 mg/cm^2 corresponds to $50 \mu\text{g/cm}^2$.

For aluminum samples with infinite thickness with respect to the beam, the activity due to $^{26}\text{Al}^m$ increases accordingly; in addition the production of ^{26}Si becomes also apparent. In this case, the determination of sulfur under the experimental conditions outlined above becomes difficult due to a complex three component decay curve.

The accuracy and precision in the sulfur determina-

TABLE 4

Reaction	Threshold	Half-life	β^+ emission	γ emission
$^{27}\text{Al}(p,n)^{27}\text{Si}$	5.81 MeV	4.1 - 4.45 sec	3.85 MeV	0.511 MeV 200%
$^{27}\text{Al}(p,d)^{26}\text{Al}^m$	11.46 MeV	6.28-6.74 sec	3.21 MeV	0.511 MeV 200%
$^{27}\text{Al}(p,2n)^{26}\text{Si}$	9.12 MeV	1.7 - 2.1 sec	3.83 MeV	0.511 MeV 200% 0.82 MeV 34%

tion can be enhanced by increasing the threshold, this will, however, result in a loss of sensitivity. Fig. 7 shows the ^{32}Cl decay curve obtained with the previously used sulfur target but with a thick aluminum backing (810 mg/cm²). The threshold setting (channel 220) is considerably higher. However, the activity recorded due to ^{32}Cl could be kept approximately constant compared to the data given in fig. 5, by increasing the beam current to 7 μA and decreasing the irradiation time thus favoring the buildup of ^{32}Cl versus the production of ^{26}Si and $^{26}\text{Al}^m$. Consequently, the data presented in

fig. 7 confirms the estimate on the detection limit given previously and extends it to thick aluminum samples. It might be noted here that further refinements of the irradiation and counting conditions for a given experimental case could result in a still lower detection limit. It should also be emphasized again that while the case of aluminum should be fairly representative for a number of matrices, the sensitivity is matrix dependent. Tantalum, for example, was found to have no short lived proton induced activity and would thus constitute a more favorable case.

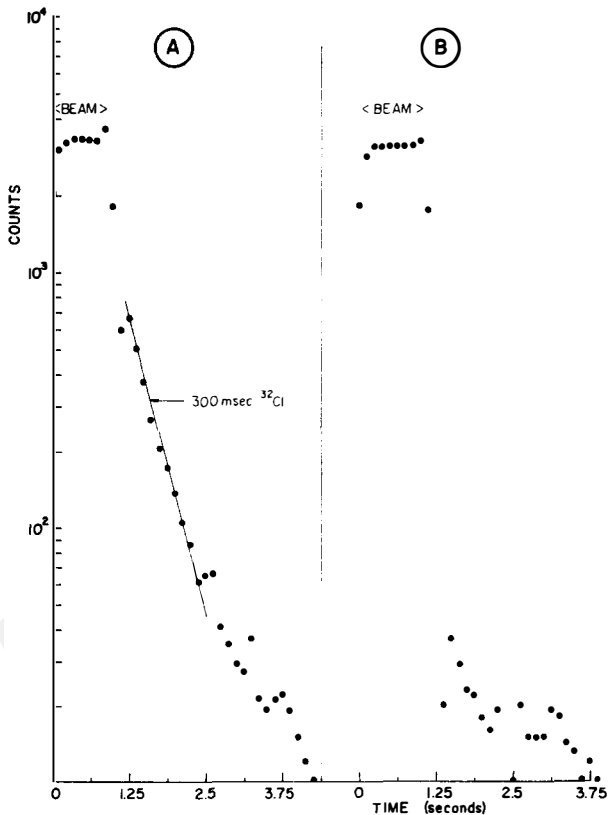


Fig. 6. Decay curves obtained (a) from a thin sulfur deposit on an aluminum foil, (b) from an aluminum foil alone.

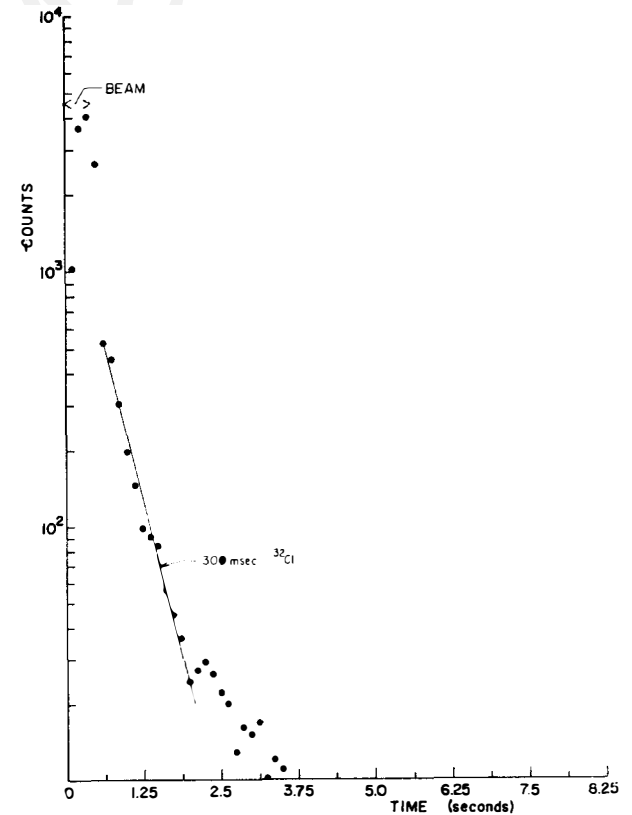


Fig. 7. Decay curve from a thin sulfur deposit on a thick aluminum backing.

3.6. DETERMINATION OF SULFUR IN CRUDE OILS

Several petroleum samples with sulfur contents varying from 3.18 to 0.72 weight percent were irradiated using the setup described earlier. On each sample the decay data was accumulated from three successive irradiations. All data was normalized against a residual fuel oil containing 2.14% sulfur supplied by NBS (Standard Reference Material No. 1622). The decay data contained a long lived component (6–7 sec) which could not be reduced by displacing the threshold. This activity has been assigned to ^{16}N produced from oxygen via an (n,p) reaction. The radiations emitted by ^{16}N (β^- of $E_{\text{max}} = 10.4$ MeV and γ -rays of 6.13 and 7.12 MeV) would indeed not allow a selective discrimination from ^{32}Cl . The formation of ^{16}N is further evidenced by data obtained on a water sample irradiated under similar conditions.

The sulfur contents determined in various crude oils are given in table 5. The average percent difference between the amounts of sulfur present and found is 12%. Improved precision could be achieved by increasing the number of repetitive irradiations on each sample.

4. Conclusion

The method presented relies on a very simple detector and counting electronics. Its performance in terms of sensitivity, selectivity, and precision depends (a) on a careful selection of the experimental conditions minimizing contributions due to other radioactive species and (b) on the size of the detector and number

TABLE 5
Sulfur contents (in weight percent)
in petroleum samples.

Sample	Present	Found
NBS	2.14	Standard
2	3.18	3.1 ± 0.15
8	2.83	2.70 ± 0.15
6	1.45	1.74 ± 0.2
7	0.95	1.15 ± 0.2
1	0.72	0.82 ± 0.2

of repetitive irradiations for obtaining a gross count rate and counting statistics deemed necessary. The distinctive features of this technique are that it is rapid, non-destructive and applicable to solid and liquid organic or inorganic materials. The Cherenkov counting of ^{32}Cl could naturally be extended to other short lived high energy positron and electron emitters thus opening possibilities for a number of other analytical applications.

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