CERIC-CUPRIC SULFATE DOSIMETER(1) *Conf-721101--1*

D. R. Longirwar*, J. Weiss**

Abstract

The ceric-cupric sulfate chemical dosimeter was investigated using cobalt-60 radiation over a dose range of 1 to 25 ~~Mrads~~^M at the following concentrations: 50 mM Ce and 100 mM Cu, 25 mM Ce and 50 mM Cu, 25 mM Ce and 1 mM Cu, 25 and 50 mM Ce with no cupric ion. Initial test and test after storage of solution for three months indicate that the G-value does not change over the specified concentration ranges.

Linearity studies indicate the following: 50 mM Ce with 100 mM Cu solutions are linear in response from 1 to 15 ~~Mrads~~^M and 25 mM Ce + 50 mM Cu solutions are linear from 1 to 8 ~~Mrads~~^M. Spectrophotometric analysis combined with dilution techniques was found to be a convenient and reliable method of analysis. The precision obtained with the system for reproducible results and measurements approached that of the Fricke dosimeter. *(puth)*

(1) Research performed under auspices of the U.S.A.E.C.

* Address: Bhabha Atomic Research Center, Trombay, Bombay, India.

** Address: Brookhaven National Laboratory, Upton, New York.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

MASTERDISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *fcg*

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Introduction

Whether one is interested in radiation processing or in radiation research, it is necessary to be able to accurately measure the amount of energy absorbed by the material being irradiated. In most cases the demand for high degrees of accuracy will not be as great in radiation processing as it is in research.

When dose measurements are made inside of absorbing media, it is important that the dosimeter selected for use possess the correct size, shape, density and atomic number relative to medium in which it is to be used. This is particularly important when the dose rate and the energy spectrum of the ionizing radiation are varying rapidly with respect to physical position inside the target. These conditions exist at great target depths and at interfaces when the radiation source is a gamma ray emitter, and throughout the target when charged particles are being used. Under these conditions an essential prerequisite for the accurate measurement of absorbed dose is that the dose response of the dosimeter match that of medium in which the measurement is being made. It is therefore of importance that the response of each dosimetry system be thoroughly understood and that a wide choice of dosimetric systems be available to the experimenter to enable him to select one that will best fit his experimental conditions. When this is not possible, a wide variety of dosimeters should be available

since, if the dosimeter is similar in density and atomic number to the medium in which it is to be used, the response of the material and the dosimeter to ionizing radiation is most likely to be similar. In radiation research dosimetry, the main problem is the accurate determination of the absorbed dose in the target materials; of secondary importance is the subsequent monitoring of the experiment.

To date the only dosimetry procedure generally accepted as a "standard" is the ASTM procedure for the Fricke dosimeter. Because this system is accurate and reliable, it is widely used as a calibration standard for absorbed dose measurements. The usefulness of this system, however, is seriously impaired both as a calibration standard and as an "in-target" dosimeter because of its limited range (up to 40,000 rads). With the need firmly established for additional dosimetry standards, great efforts to develop and use different dosimeters are being made. The ceric sulphate dosimeter and other chemical dosimeters were used and tried by various workers to attain simplicity and accuracy in estimations and measurements of various dose ranges.

The ceric dosimeter can be used to measure doses in the range 0.1⁽¹⁾ to 100 Mrads⁽²⁾. It has very good stability before and after irradiation, ⁽²⁾ is independent of dose rate over a wide range, ⁽¹⁾ has well defined reaction mechanism⁽³⁾ and the cerium (n) reduced is readily measurable. The I.C.R.U.⁽⁴⁾ rated it next in

usefulness to the Fricke dosimeter and as a reference standard for doses higher than 5×10^4 rads. A precision of $\pm 2\%$ is possible when great care is taken. ⁽¹⁾

However, the most serious disadvantage of the method in routine dosimetry is its extreme sensitivity to impurities, shown by high and non-reproducible reduction yields. ^(1,5,6,7)

Purity of solutions and cleanliness of apparatus must be ensured.

Triple distillation of water and aging of the dosimeter solution in the presence of the glassware to be used are essential to the attainment of reliable results. ⁽⁴⁾

Nevertheless, its dose range makes it a prospective dosimeter in sterilization of foods ⁽⁸⁾ and pharmaceuticals, and in other megard irradiation processes.

Clark and Coe in 1937 ⁽⁹⁾ briefly studied the effects of addition of Ag^+ , Hg^{+2} , and Cu^{2+} on the ceric system; and Taymuty, Towle and Peterson ⁽¹⁾ have mentioned attempts to stabilize the system

using a stronger oxidant than ceric sulfate. A more direct effort

to improve the system was made by Munoz and Miro ⁽¹⁰⁾ who studied

the effect of the addition of cupric sulfate. They concluded

that the presence of 100 mM Cu^{2+} resulted in a general stabiliza-

tion of the system, giving reproducible results with singly distilled water.

In some respects the ceric-cupric dosimeter is potentially a more useful system and is generally accepted as the standard

chemical dosimeter. The broad dose range, simplicity of analysis and dose rate insensitivity are all equal or superior to other chemical methods. The system has been used to measure doses as low as 50 rads^(11,12) and as high as 100 Megarads.⁽²⁾ It can be readily analyzed using titration or spectrophotometry, and is insensitive to dose rates up to 10^{11} rads per second.⁽¹³⁾ Of particular interest is its relatively constant (G) value irrespective of concentration of the dosimetric solution.

The ceric/cupric system was studied over a wide dose range using various concentrations of ceric and cupric ion. This report describes the results of the study.

Experimental

Materials

Ceric and cupric sulfate including sulfuric acid used were ACS Reagent Grade.

The radiation source was BNL cobalt-60 tube facility type containing approximately 60,000 Curies of cobalt-60 surrounding a 4" diameter tube. The irradiation vessels were flame sealed ampoules of nominal five milliliter volume. These ampoules were thoroughly cleaned, sterilized and rinsed with the dosimetric solution before filling. Dilutions were performed using 0.8N sulphuric acid prepared in triple distilled water.

The irradiation of ampoules was carried out by putting the same in a holder. The holder was lowered and placed in center of the tube type facility. As a result ampoules were irradiated under identical conditions every time. For each exposure, two ampoules were irradiated to compensate for non-uniformity of the radiation field and uncertainties in positioning of the holder. The measured dose was taken as the average of two samples.

All spectrophotometric readings were made on a Model DU spectrophotometer from Beckman Instruments. The spectrophotometer was equipped with a temperature controlled cell compartment for absorbance measurements.

Methods

Stock solutions containing 50 mM Ce^{4+} and 100 mM Cu^{2+} solution were prepared by adding weighed amounts of $\text{Ce}(\text{HSO}_4)_4$ and $\text{Cu}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$ in 0.8N sulfuric acid. Ceric sulfate solution was allowed to stand for two to three weeks without being disturbed. The ceric sulfate solution was then passed through Whatman No. 12 fluted filters. To prepare the dosimetric solutions an appropriate quantity of 50 mM Ce^{4+} was taken and weighed amounts of $\text{Cu}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$ was added to it so that a dosimetric solution of 50 mM Ce^{4+} + 100mM Cu^{2+} was prepared. Similarly, 25 mM Ce^{4+} + 50 mM Cu^{2+} and 50 mM Ce^{4+} and 25 mM Ce^{4+} solutions were prepared. Also to an appropriate quantity of 25 mM Ce^{4+} sol. weighed amt. of $\text{Cu}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$ was added to prepare 25 mM Ce^{4+} + 1 mM Cu^{2+} solution.

All these solutions were filled in different ampoules and were subjected to radiation from 1 Megarad to 25 Megarad except in the case of solutions containing 25 mM Ce^{4+} concentration. In order to simplify the measurement of the irradiated ceric/cupric solutions, a spectrophotometric method was desirable.

A possible source of error in the ceric/cupric method is the additional spectrophotometric reading required for the blank. To reduce this error, a minimum of two blanks were used for each exposure. They were prepared, handled and analyzed in the same manner as the samples. Their absorbance were averaged to determine the change in absorbance for each of the samples. No precautions were taken to shield solutions from laboratory lighting. Dilution factors were selected which gave the widest possible dynamic range for each concentration, consistent with limitations of the spectrophotometric system. The absorption of the blanks were held in the range of 1.0 to 1.3 O.D. units by using spacers in the cuvettes of the spectrophotometer which reduces the reading by a factor of ten.

Results

Optical densities of the irradiated dosimetric solutions were recorded after dilution and/or using spacers. Optical densities of unirradiated solutions were also recorded. Difference in optical densities of blank and irradiated solution for different dosages was also recorded (Table 1, 3 and 3A). A graph (Fig. 1)

of different solution concentrations and change in their optical densities was plotted to see the effect of adding copper ions in the dosimetric solution viz. ceric sulfate. Since, by definition, the G value of a reaction is simply the rate of change in the system with respect to the energy absorbed, this method provides the most precise results. The two samples from each exposure were averaged and the resulting values determine the line or curve which fitted the data most accurately. In all cases, a linear relationship of the form $y = a + b x$ was found to be observed when differences in optical densities were plotted against doses administered. The slope of this line when converted to the proper units is the reported G value (2.50). Exposures which resulted in less than 5% ceric reduction, together with those analyzed at an absorbance greater than 1.3, were excluded because of their tendency to give a greater error. Fig. 2 and 3 show plots of the data for different ceric + cupric concentrations vs. the dose calibrated by Fricke dosimeters.

Conclusions

From the results obtained and the observations by Munoz and Miros, it can be said that the ceric/cupric dosimeter could be an accurate and reliable method for the determination of absorbed dose over a broad exposure range. Even though much dilutions were required for reading the optical densities of the irradiated solutions. It is expected that, with somewhat more careful control of the conditions viz. dilution, preparation of solution and measurements of optical densities, better precision could be obtained. Contrary to Munoz and Miros' work, the G value of the solution remains the same despite varying the copper concentration. The dosimetric system can be reliably used for higher dose determinations and the solution has been found to be quite stable for a period of three months. The results obtained (Table 2, 4 and 4A), after storage for such a long time, are quite consistent and indicate that this dosimeter can be stored and used for determining dosage up to 15 Megarads with good accuracy. As a result this dosimeter could be effectively and easily used in radiation processing of foods where higher dosage of 1 to 6 Megarads are administered.

TABLE 1

50 mM Ce ⁴⁺ Solution		
Dose	Blank O.D.	Δ OD
1 Mrad	1.307	5.724
2 Mrad		5.85
3 Mrad		8.52
4 Mrad		11.85
5 Mrad		13.59
8 Mrad		19.89
10 Mrad		20.41
15 Mrad		34.87
20 Mrad		39.109
25 Mrad		39.113

50 mM Ce ⁴⁺ + 100 mM Cu ²⁺		
Dose	Blank O.D.	Δ OD
1 Mrad	1.301	1.74
2 Mrad		3.75
3 Mrad		6.85
4 Mrad		9.12
5 Mrad		11.34
8 Mrad		18.24
10 Mrad		18.87
15 Mrad		32.43
20 Mrad		38.89
25 Mrad		38.82

25 mM Ce ⁴⁺ Solution		
Dose	Blank O.D.	Δ OD
1 Mrad	1.29	3.34
2 Mrad		6.98
4 Mrad		13.44
5 Mrad		15.84
8 Mrad		21.54
10 Mrad		25.45
15 Mrad		25.72
20 Mrad		25.73

25 mM Ce ⁴⁺ + 50 mM Cu ²⁺		
Dose	Blank O.D.	Δ OD
1 Mrad	1.26	3.6
2 Mrad		5.5
4 Mrad		11.78
5 Mrad		14.85
8 Mrad		15.31
10 Mrad		24.87
15 Mrad		25.121
20 Mrad		25.130

25 mM Ce⁴⁺ + 1 mM Cu²⁺ Solution

Dose	Blank O.D.	Δ OD
1 Mrad	1.23	3.02
2 Mrad		6.13
4 Mrad		12.55
5 Mrad		15.38
6 Mrad		18.48
8 Mrad		20.07
10 Mrad		24.19

TABLE 2

Readings taken after storage of solution for about three months.

(All readings were taken in duplicate.)

50 mM Ce ⁴⁺ Solution		
Dose	Blank O.D.	Δ OD
1 Mrad	1.3069	5.721
2 Mrad		5.84
3 Mrad		8.49
4 Mrad		11.87
5 Mrad		13.61
8 Mrad		20.01
10 Mrad		20.50
15 Mrad		34.87
20 Mrad		39.109
25 Mrad		39.114

50 mM Ce ⁴⁺ + 100 mM Cu ²⁺		
Dose	Blank O.D.	Δ OD
1 Mrad	1.302	1.75
2 Mrad		3.76
3 Mrad		6.86
4 Mrad		9.13
5 Mrad		11.35
8 Mrad		18.26
10 Mrad		18.90
15 Mrad		32.45
20 Mrad		38.90
25 Mrad		38.86

25 mM Ce ⁴⁺		
Dose	Blank O.D.	Δ OD
1 Mrad	1.299	3.35
2 Mrad		7.0
4 Mrad		13.45
5 Mrad		15.85
8 Mrad		21.58
10 Mrad		25.46
15 Mrad		25.75
20 Mrad		25.76

25 mM Ce ⁴⁺ + 50 mM Cu ²⁺		
Dose	Blank O.D.	Δ OD
1 Mrad	1.259	3.5
2 Mrad		5.51
4 Mrad		11.79
5 Mrad		14.86
8 Mrad		15.32
10 Mrad		24.869
15 Mrad		25.122
20 Mrad		25.131

TABLE 3

50 mM Ce⁴⁺

No.	Dose (Mrad)	Time of Irradiation		Dilution Factor	O.D.
		Min.	Sec.		
1	1	7	42	20 to 1	1.1162
2	2	15	24	20 to 1	1.112
3	3	23	6	20 to 1	1.023
4	4	30	48	20 to 1	0.912
5	5	38	30	20 to 1	0.854
6	8	61	36	10 to 1	1.278
7	10	77	-	10 to 1	0.940
8	15	115	30	10 to 1	0.217
9	20	154	-	As is	0.101
				Undiluted	
10	25	192	30	As is	0.097
				Undiluted	

50 mM Ce⁴⁺ + 100 mM Cu²⁺

No.	Dose (Mrad)	Time of Irradiation		Dilution Factor	O.D.
		Min.	Sec.		
1	1	7	42	20 to 1	1.243
2	2	15	24	20 to 1	1.176
3	3	23	6	20 to 1	1.106
4	4	30	48	20 to 1	0.997
5	5	38	30	20 to 1	0.923
6	8	61	36	10 to 1	0.693
7	10	77	-	10 to 1	1.008
8	15	115	30	10 to 1	0.330
9	20	154	-	As is	0.133
				Undiluted	
10	25	192	30	As is	0.207
				Undiluted	

TABLE 3A

25 mM Ce⁴⁺

No.	Dose (Mrad)	Time of Irradiation		Dilution Factor	O.D.
		Min.	Sec.		
1	1	7	42	10 to 1	1.123
2	2	15	24	10 to 1	0.941
3	4	30	48	10 to 1	0.618
4	5	30	30	10 to 1	0.249
5	8	61	36	No dilution Reading with Spacers	0.426
6	10	77	-	No dilution Reading with Spacers	0.035
7	15	115	30	As is Undiluted	0.05
8	20	154	-	As is Undiluted	0.07

25 mM Ce⁴⁺ + 50 mM Cu²⁺

No.	Dose (Mrad)	Time of Irradiation		Dilution Factor	O.D.
		Min.	Sec.		
1	1	7	42	10 to 1	1.080
2	2	15	24	10 to 1	0.985
3	4	30	48	10 to 1	0.671
4	5	38	30	10 to 1	0.517
5	8	61	36	No dilution Reading with Spacers	0.989
6	10	77	-	No dilution Reading with Spacers	0.033
7	15	115	30	As is Undiluted	0.078
8	20	154	-	As is Undiluted	0.070

TABLE 4

Readings taken after storage of solution for about 3 months.

50 mM Ce⁴⁺ Solution

No.	Dose (Mrad)	Time of Irradiation		Dilution Factor	O.D.
		Min	Sec		
1	1	7	53	20 to 1	1.16
2	2	15	46	20 to 1	1.112
3	3	23	39	20 to 1	1.023
4	4	31	32	20 to 1	0.911
5	5	39	25	20 to 1	0.856
6	8	63	4	10 to 1	0.959
7	10	78	50	10 to 1	0.935
8	15	118	15	10 to 1	0.216
9	20	157	40	As is Undiluted	0.098
10	25	197	5	As is Undiluted	0.093

50 mM Ce⁴⁺ + 100 mM Cu²⁺

No.	Dose (Mrad)	Time of Irradiation		Dilution Factor	O.D.
		Min	Sec		
1	1	7	53	20 to 1	1.245
2	2	15	46	20 to 1	1.210
3	3	23	39	20 to 1	1.073
4	4	31	32	20 to 1	1.03
5	5	39	25	20 to 1	0.923
6	8	63	4	10 to 1	0.693
7	10	78	50	10 to 1	1.008
8	15	118	15	10 to 1	0.330
9	20	157	40	As is Undiluted	0.160
10	25	197	5	As is Undiluted	0.200

(Time of irradiation was changed by taking into account decay of cobalt-60 source.)

TABLE 4A

Readings taken after storage of solution for about 3 months.

25 mM Ce⁴⁺

No.	Dose (Mrad)	Time of Irradiation		Dilution Factor	O.D.
		Min	Sec		
1	1	7	53	10 to 1	1.121
2	2	15	46	10 to 1	0.939
3	4	31	32	10 to 1	0.616
4	5	39	25	10 to 1	0.496
5	8	63	4	No dilution Reading with Spacers.	0.420
6	10	78	50	No dilution Reading with Spacers.	0.032
7	15	118	15	As is Undiluted	0.03
8	20	157	40	As is Undiluted	0.02

25 mM Ce⁴⁺ + 50 mM Cu²⁺

No.	Dose (Mrad)	Time of Irradiation		Dilution Factor	O.D.
		Min	Sec		
1	1	7	53	10 to 1	1.084
2	2	15	46	10 to 1	0.983
3	4	31	32	10 to 1	0.669
4	5	39	25	10 to 1	0.516
5	8	63	4	No Dilution Reading with Spacers.	0.986
6	10	78	50	No Dilution Reading with Spacers.	0.031
7	15	118	15	As is Undiluted	0.058
8	20	157	40	As is Undiluted	0.059

(Time of Irradiation was changed by taking into account decay of cobalt-60 source.)

REFERENCES

1. Taimuty, S. I., Fowle, L. H. and Peterson, D. L.
Nucleonics, 17, 103 (1959).
2. Harlan, J. T. and Hart, E. J., Nucleonics, 17, 102 (1959)
3. Sworski, T. J., Radiation Research 4, 483 (1956).
4. International Commission on Radiological Units and Measurements, Natl. Bur. Stds., Handbook 85 (1964).
5. Hart, E. J., Koch, H. W., Petrie, B., Schulman, J. H.,
Taimuty, S. I., and Wyckoff, H. O., II U.N. Intern.
Conf. Peaceful Uses of Atomic Energy, 21, 188 (1958).
6. Barr, N. F. and Schuler, R. H., J. Phys. Chem. 63, 808, (1959).
7. O'Leary, B. M., Unpublished A.A.E.C. Tech. Note (1964).
8. Holm, N. W., Symp. on the Utilization of Large Radiation
Sources and Accelerators in Industrial Processing,
Munich, Germany (1969).
9. Clark, G. L. and Coe, W. S., J. Chem. Phys. 5, 97 (1937).
10. Manoz, F. J. and Miros, M., Intern. Jn. Appl. Radiation and
Isotopes, 15, 153 (1964).
11. Hardwick, T. J., Canadian J. Chem. 30, 23 (1952).
12. Frigerio, N. A. and Henry, V. D., Solid State and Chemical
Rad. Dosimetry in Med. and Biol., Intern. A.E.A.,
Vienna, Austria, 257-266 (1967).
13. Taimuty, S. I., Towle, L. H. and Peterson, D.L., Ibid 103.

832 0

Concentration

NEUFEL & ISSER CO.

AL
-17V
5.1E
↑

CLIFFORD & LUTHER CO.