The establishment of a portable high sensitivity exhaled thoron activity measurement system

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Abstract A portable system, using electrostatic collection, for the measurement of exhaled thoron activity in humans is described, together with the basic theory, equipment, calibration procedures, measurement and the preliminary use. The portable system built on experience at the Argonne National Laboratory to achieve a reduction in measurement time from 30 hours to 200 minutes, and to increase the total efficiency of the system from 50%(ANL) to 55% with a minimum detection limit decreased to 0.007Bq (zero activity±2σ). The total standard error of this system is 47% for a thorium lung burden of 0.22Bq. The average background of this scintillation detector was 0.003 counts/min.

Keywords: Thorium-daughter-products; Thoron, Electrostatic collection, Scintillation detectors.

1. Introduction

The measurement of exhaled thoron is much more sensitive and much simpler than whole body counting for the assessment of the thorium content of the human body. Based on the work of Keane and Brewster[1] at Argonne National Laboratory (ANL), ANL's system was modified and improved by us to increase it's sensitivity by a factor of 20 as compared with the original one (scintillation flask method)of our laboratory[2] and to achieve background levels and a total efficiency that slightly better than that of the ANL system. At the Bayun Obo Rare-earth Iron Mine the modified system is used for the following purposes: for detecting thorium contamination in the human body; investigating dose-effect relationships in the miners inhaling thorium-containing dusts; calculating the dose received from the thorium compounds in the target tissues of miners, and assessing the efficiency of comprehensive protection methods. The main objective of this report is the first time to present the characteristics of this improved system systematically, including the development of the device, the calibration process, the collection ;and measurement exhaled thoron, the total error of the measurements and the assessment of the method.

2. The characteristics of the improved system

In the ANL system, sample counting was performed automatically with the help of a computer, and the counting time was around 30 hours. Since no computer was available at the mine in 1982, a simplified sample counting method, using a calculator, was established which permitted a decrease in counting time. to 200 minutes[3]. Instead of an automatically controlled respirator to change the pulse-like expiration air flow into a stable one, two aluminium single–directional valves combined with a tri-directional instrument connected to the mask was used; the latter was much cheaper.
The high negative voltage used by this system was increased from 5.8 kV to 9.0 kV, which was the critical step for increasing the total-efficiency of the measurement system from 50 % to 55%[3]. In addition the whole system was changed from a stationary one to a portable one.

2.1. The measurement system

The apparatus consists of two parts, the exhaled thoron daughter-product collector and the radiation detector
The electrostatic collection system consists of a cylindrical steel tank of 36.8 liters in capacity fitted

with a removable electrode in its top. A 0-10 kV high-voltage power supply is connected to the top of the electrode, and at the lower end a copper electrode can be swung into place. The copper electrode in covered with a Mylar disk coated with a zinc sulphide phosphor (ASP-415/16 α). A face mask and aluminium respiratory set with a three-way valve is connected to the inlet tube to the tank. The outlet tube from the tank leads through a three-way valve to a rubber bag and a wet test meter to a vacuum pump.
The detector consists of a Lucite holder mounted on the window of a 9836 KA low dark current photomultiplier. The photomultiplier is connected to an FH-454 Automatic scaler and a power supply with a manostat.

2.2. Procedure

The copper disk electrode maintained at a negative potential of 9.0 kV with respect to the walls of the container. The copper electrode in covered with a Mylar disk coated with zinc sulphide phosphor. For an average breathing rate of 7.5 l/min the breath stays in the chamber almost 5 minutes and its thoron content decays almost completely (~97%), producing ^{212}Pb ($T_{1/2}$ 10.6 hours). The positively charged particles collected on the negatively charged electrode. At the end of breath sampling (usually 50 minutes), the electrode is removed and covered with a second disk of Mylar coated with zinc sulphide placed in the Lucite holder on the photomultiplier assembly. A period of 4 hours is allowed for the decay of short-lived radon daughters, before the α-counting begins for a counting time of 200 minutes. In this way the alpha particles from the ^{212}Pb daughters are counted with almost 100% efficiency (4π geometry). Figure 1 illustrates the theory of the collection process (The ^{228}Th decay scheme).

1. $^{228}Th \xrightarrow{\alpha} {}^{224}Ra \xrightarrow{\alpha} {}^{220}Rn$ ($T_{1/2}$ = 55.6 Sec.)
2. $^{220}Rn \xrightarrow{\alpha} {}^{216}Po \xrightarrow{\alpha} {}^{212}Pb \xrightarrow{\beta} {}^{212}Bi \xrightarrow{\beta} {}^{212}Po$

($T_{1/2}$=10.6 hrs.) ↓α ↓α

$^{208}Tl \xrightarrow{\beta} {}^{208}Pb$

Of the newborn ^{212}Pb 85—88% of the atoms have a positive charge

Figure 1. The ^{228}Th decay scheme

The counts are corrected for radioactive decay and for the counting efficiency, and the ultimate result is expressed as the activity of freely emanating radium-224 at the mouth of the subject.

2.3. The calibration process

The total efficiency is the product of three fractions: the proportion of the exhaled thoron atoms that decay in the collection chamber; the fraction of ^{212}Pb produced in the chamber that decays on the phosphor disk (the collection efficiency) and the fractional efficiency of the α-scintillation counter. Before calibration the optimal working conditions of the scintillation counter are determined using a ^{239}Pu source. Then the Lucite holder, fitted with a clean copper electrode, is placed on the upper side of the photomutiplier to measure the background of the counter. When measurements were carried out for 8 hours per day over a ten-day period the average background was 0.003±0.00025 counts per minute, or 4-5 counts per 24 hours. The next step is to determine the optimal high voltage for the collection by measuring the de-emanation of a ^{232}Th solution (38.4Bq), at a flow rate of 1.2 l/min over 50minutes, with different negative high voltages. From the relationship between the collection efficiency and the voltages shown in Table 1, a value of 9.0kV was selected.

Table 1. The collection efficiencies for thoron progeny at different negative high voltages.

Negative high voltage (kV)	Relative collection efficiency* (±S.E.)
0	
3.0	0.40±0.012
5.0	0.36±0.011
6.0	0.43±0.012
7.0	0.69±0.017
8.0	0.76±0.018
9.0	0.89±0.02
9.8	1.00

*Errors reflect the counting errors only.

After the optimal conditions were established, the overall efficiency, E, was calculated using the equation:

$$E=f_\lambda f_c \eta \qquad (1)$$

Where f_λ is the fraction of exhaled thoron atoms that decay in the collection chamber, f_c is the fraction of the ^{212}Pb produced in the chamber that decays on the phosphor disk (collection efficiency), and η is the fractional counting efficiency[2].

If it is assumed that there is no mixing of incoming air with that already in the collection apparatus (i.e. there is a smooth flow), the fraction of exhaled thoron atoms, f_s, that survives decay in the mask and tubing and is delivered to the collection chamber is obtained from the equation of Evans [4].

$$f_S = e^{-\lambda v/R} \qquad (2)$$

Where λ is the radioactive decay constant of thoron (0.76 min^{-1}), v is the air volume of the mask and tubing leading from the mask to the chamber, and R is the flow rate.

The fraction f_D of thoron atoms delivered to the chamber that decay in the chamber is calculated using the formula of Evans[4]:

$$f_D = 1 - e^{-\lambda V/R} \qquad (3)$$

Where V is the volume of the collection chamber; f_λ is the product of f_S and f_D, so that, for smooth flow:

$$f_\lambda = e^{-\lambda v/R} - e^{-\lambda(v+V)/R} \qquad (4)$$

The expression f_λ multiplied by 0.815 and by the activity of ^{232}Th standard solution in the emanating bottle gives the effective activity of freely emanating ^{224}Ra; 0.815 is the fractional de-emanation efficiency at a flow rate of 1.2 L/min as estimated by Kuchta et al[5].

Then, using the Equation 5, the total efficiency E is obtained:

$$B\lambda_B = FXE(1 - e^{-\lambda_B t}) \qquad (5)$$

Where B is an estimate of the number of ^{212}Pb atoms on the electrode phosphor at the end of the collection period t and where F is the fraction of thoron atoms produced from the decay of ^{224}Ra in the body that is exhaled, X is the total ^{224}Ra activity in the body, E is the overall efficiency of the collection and counting apparatus, and λ_B is the radioactive decay constant of ^{212}Pb, 1.82×10^{-5} sec^{-1}. $B\lambda_B$ is the activity of ^{212}Pb precipitated on the surface of the ZnS phosphor on the copper disk. The measurement results are expressed by the thoron outside the body, which is equivalent to FX in equation (5). The total efficiency is determined by a series of respiratory minute-volumes.

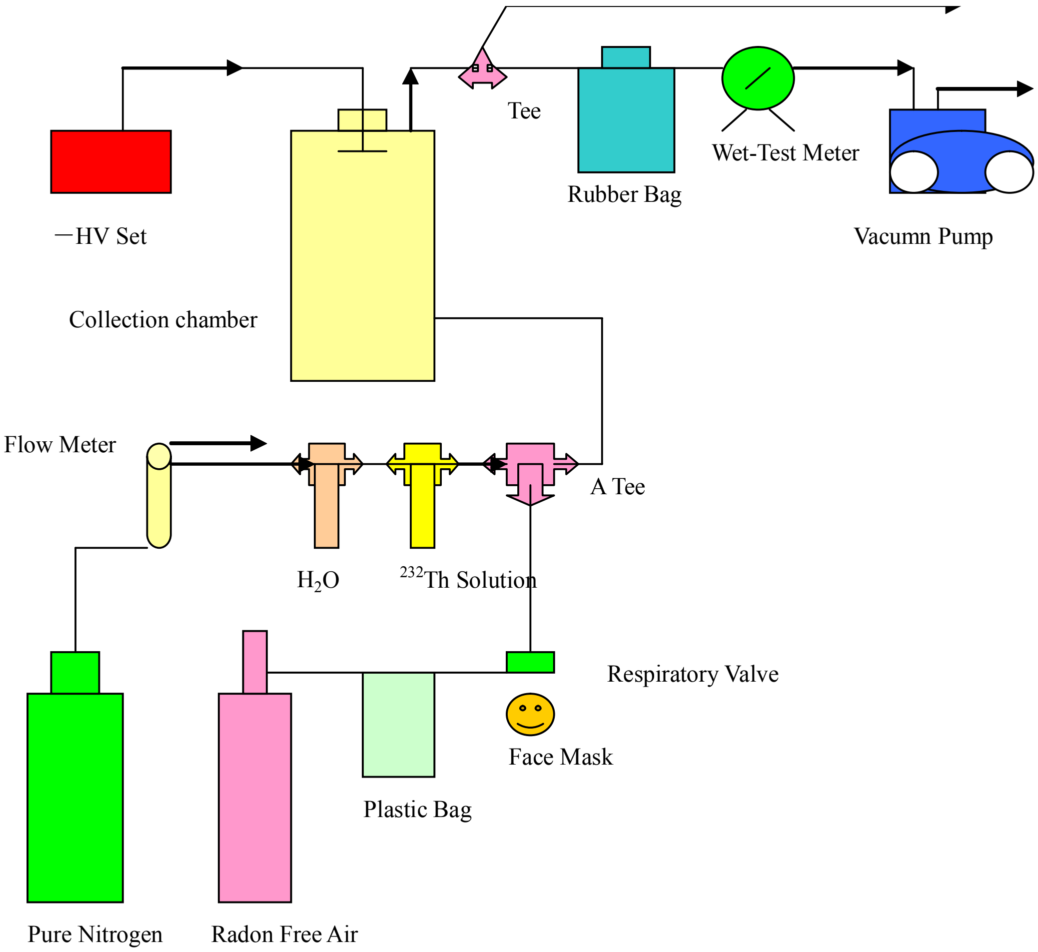

Figure 1 The apparatus used for collecting exhaled thoron progeny and the thoron emanating set used in calibration, the latter connected with the former in point A.

The calibration process needed to obtain the total efficiency E is carried out as follows: the calibration source is a 250-ml de-emanation bottle, containing 24.90mg. (101.4 Bq) thorium (^{232}Th in secular radioactive equilibrium with ^{228}Ra, ^{228}Th and ^{224}Ra), dissolved in 100ml. 1 M HCl.
To start the calibration, thoron is transferred to the collection apparatus by bubbling aged air through the solution in the de-emanation bottle at a rate of 1.21/min. for 5 minutes. After that the expiration tube from a normal person wearing a mask inhaling aged air is connected to the middle inlet of the tee-valve. The high voltage, 9.0kV, and the pump are then turned on simultaneously, in order to let the normal subject exhale into the collection apparatus. The thoron-bearing de-emanating air is mixed with the normal subject's exhaled air at point A (Fig 1); after 15 minutes the high voltage is turned off and the total airflow volume is registered. The copper disk from the electrode is placed in the Lucite holder, on the top of the photomultiplier for 4 hours. After that, the α-activity is measured by counting for 200 minutes.
By substituting the total counts into the following formula recommended by Keane [1] , the unknown E will be available.

$$\text{Total Counts} = (Tn)\,(E_T)\int_{t_1}^{t_2}(ThA + ThC\,)dt$$

$$= (Tn)(E\,)[53.76(e^{-0.00109t_1} - e^{-0.00109t_2}\,) - 4.026(e^{-0.0114t_1} - e^{-0.0114t_2}\,)] \qquad (6)$$

Where, Tn is the thoron activity outside the body; E is the total efficiency; t_1 is the time from the beginning of exhaled air sampling to the end of sampling (minutes); t_2 is the time from the end of exhaled air sampling to the end of sample counting (minutes). Equation (6) was derived with a 50-minute exhaled air sampling period; the exhaled air collection time was 15 minutes, the parameters in Equation (6) were then changed as shown in Equation (7):

$$\text{Total Counts} = (Tn)(E)[16.4578(e^{-0.00109t_1} - e^{-0.00109t_2}) - 1.458(e^{-0.0114t_1} - e^{-0.0114t_2})] \quad (7)$$

In addition, the formula recommended by Keane, also gives the ratio between the activity of ThB on the electrode relative to the activity of ^{220}Rn, with an exhaled air collection time of 50 minutes.

$$\frac{ThB}{Tn} = 1 + 0.0000042\ e^{-260(50)} - 1.0000042\ e^{-0.00109(50)} = 1 - e^{-0.00109(50)} = 0.0530 \quad (8)$$

When the exhaled air sampling time is 15 minutes, the formula (8) should be changed to:

$$\frac{ThB}{Tn} = 1 + 0.0000042\ e^{-260(15)} - 1.0000042\ e^{-0.00109(15)} = 1 - e^{-0.00109(15)} = 0.016 \quad (9)$$

Thus, by combining Equations 9 and 7, a simple formula for the relationship between the total counts E and the activity of ThB is obtained, provided the total counts are known. Putting the simple formula into Equation 5, the real value of total efficiency is obtained.
Based on 11 experiments (7 of them combined with human expiration), the E values shown in Table 2 were obtained.

Table 2. Under the condition of 8 average flow rate equals R (experiment value), the total efficiency E, expected value of fx and the derived value of $f_c\eta$ are obtained.

R (L/min.)	E [a] (Observed)	f_λ (Expected) [b]	$f_C\eta$ (col.2÷col.3.)	E (Adjusted) [c]
	0.50			
1.2	0.56	0.76	0.69±0.025	0.45±0.017
	0.48			
	0.55			
6.53	0.53	0.94	0.56	0.52
7.02	0.56	0.94	0.60	0.55
9.94	0.54	0.91	0.59	0.53
5.91	0.54	0.94	0.57	0.52
4.74	0.58	0.93	0.62	0.56
8.67	0.56	0.92	0.61	0.55
10.96	0.60	0.89	0.67	0.59
mean（n =7）			0.60	0.55
standard error (S.E)			0.014	0.010
standard deviation (S.D)			0.037	0.025

Table 2 showed that the Average Value of E after adjustment is 0.55*

a E、f_λ and $f_c\eta$ are all dimensionless

b According to formula: $f_\lambda = e^{-\lambda v/R} - e^{-\lambda(v+V)/R}$

（v=0.43L，V=36L）

c Adjusted value of E=column 2× $e^{-0.76\times0.23}$ L /R (L/min)

Here, 0.23L is the free volume of the mask to chamber hose between the point of deemanated Tn (A Tee in Fig 2-3) and the chamber inlet.

2.4. The collection and measurement of exhaled thoron

Before applying the 9.0 kV voltage to the electrode of the collection apparatus, the subject inhales radon-free air and exhales into the collection apparatus for 15 minutes, in order to decrease the activity of thoron gas in the subject's lung inhaled from the environment, also to exchange the air inside the collection apparatus. Immediately after this 15 minutes' air exchange is ended, the 9.0 kV-voltage is applied to the electrode. The thoron progeny are then collected on the copper electrode for 50 minutes, after which time the copper electrode is placed into the Lucite holder. Four hours later the Lucite holder is placed on the surface of the scintillation tube and the total α-counts are registered for 200 minutes. After subtracting the background counts of the Lucite holder, the remaining counts are inserted into Equation (6), to yield the ^{224}Ra activity in the exhaled air of the examinee. Stehney [6] reported that the average ratio of emanating radium-224 to retained bismuth-212 is 0.101. Based on this ratio, the ^{212}Bi activity in the thorax can be obtained from the ^{224}Ra activity in the mouth of the subject. By adding the activity of ^{212}Bi and ^{224}Ra together, the ^{232}Th activity in the lung of the subject is obtained. In other words, a conversion factor of 3.7 Bq emanating ^{224}Ra equivalent activity at the mouth to 37 Bq ^{232}Th was used to estimate the thorium lung burden. The true amount of thorium in any case will tend to be higher[7], because there may have been insufficient time for equilibrium between thorium and ^{212}Bi to be established, because intermediate members of the decay chain, particularly ^{228}Ra and ^{224}Ra, may have left the thorium in the lungs, and also because of exhalation of ^{220}Rn. In our system the under- estimation may be as large as a factor of 2.

2.5. The total error of the measurements

The results obtained by this method include three sources of error: counting errors, the median coefficient of variation of thoron activity outside the body, and the relative systematic error of the total efficiency E.

Based on the total counts, background counts and the total measurement time, the measurement counting error can be calculated.

Based on repeat measurements of exhaled thoron activity made in 9 thorium-containing dust exposed miners from the Bayun Obo Iron Mine, the median coefficient of variation of thoron activity outside the body was ±17% (Table 2). This value is approximately the same as the value of ±15% obtained at ANL.

The relative standard error (±3.7%) of the distribution of $f_c\eta$ (Table 2) was expressed as the relative systemic standard error of the total efficiency E. the total standard error of a single measurement of thoron activity outside the subject's body is:

$$[(0.17)^2+(0.037)^2+C^2]^{1/2} FX \qquad (10)$$

where C is the percent standard error of the α-particle counting result; FX is the thoron activity outside the body. Using the above equation, the total error amounts to ±47%, with a thorium lung burden of 0.22Bq .

3. Assessment of the method

A total of 1301 measurements of exhaled thoron activity, carried out at Bayun and other places in China[8], showed that this method has two characteristics: its sensitivity high and its quite good stability. The results of the measurements carried out in 1983 (Table 3) reflect the high sensitivity, because they show that the ^{224}Ra activity at the mouth of the miners and the mine controls were really did exceed that of laboratory workers with no history of exposure to thorium dust.

The coefficients of variation (c.v.) for the measurement of exhaled thoron by 9 miners from the Bayun Obo Mine are listed in Table 4. The interval between the two measurements of each miner was 1~6 weeks. This coefficient represents the variability of the exhaled thoron with time. The median cv of the data in Table 3 was 0.17, which is higher than the 0.15 observed at ANL but our figure shows that the system is quite stable, and that the repeatability of the measurements is good.

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Table 3 The measurement value of exhaled thoron activity of 162 persons (173 person measurements)

Name of mine	number of workers	Weighted mean of emanating radium ^{224}Ra at the mouth （M±S.E.）Bq
Bayun Obo Mine	130 dust-exposed miners	0.079 ±0.0012
Bayun Obo Mine area	10 controls (incl. 5 smokers)	0.029 ±0.0062
Kabuqi Limestone Mine	6 dust-exposed miners (incl. 4 smokers)	0.016 ±0.0118
Beijing Laboratory	16 controls (27 person measurements incl 7 smokers)	0.017 ±0.0089

Table 4. The result of median variance coefficient (c.v.)of thoron activity outside the body of 9 miners of Bayan Obo Mine

Subject	Date	Free emanating ^{224}Ra at the mouth (Bq)	Variance coefficient
A	1983.8.19 1983.9.19	0.067±0.015 0.057±0.014	c.v.=0.0068/0.062=0.11
B	1983.8.04 1983.9.19	0.085±0.017 0.059±0.015	c.v.=0.018/0.072=0.25
C	1983.8.09 1983.9.19	0.090±0.018 0.172±0.023	c.v.=0.058/0.131=0.44
D	1983.8.23 1983.9.20	0.190±0.024 0.163±0.023	c.v.=0.019/0.177=0.11
E	1983.8.04 1983.9.20	0.103±0.018 0.073±0.015	c.v.=0.021/0.088=0.24
F	1983.8.24 1983.9.20	0.097±0.018 0.124±0.020	c.v.=0.019/0.110=0.17
G	1983.8.09 1983.9.20	0.069±0.015 0.051±0.013	c.v.=0.013/0.060=0.21
H	1983.8.06 1983.9.20	0.063±0.014 0.076±0.016	c.v.=0.0086/0.069=0.12
I	1983.9.20 1983.9.26	0.036±0.011 0.033±0.011	c.v.=0.0021/0.035=0.06

In order to make further assessment on the technical quality of method, a comparison between the related parameters of the new method with those from the scintillation flask method established by us in 1979, and that used by ANL, is shown in Tables 5 and 6 respectively[9].

Table 5. A comparison of the sensitivity and other characteristics of the electrostatic collection and FD-125 scintillation flask methods for the measurement of thorium lung burdens.

Method	Establishmen ttime	Background of counter [counts/min]	The total detection error for various ^{228}Th lung burdens (Bq)	Total measuremen t time [min]
Electrostatic collection	1983	0.003	0.37±0.14 0.22±0.104	200
FD-125 Scintillation flask	1979	0.40	4.44±2.36 2.22±2.11	30

Table 5 shows that the overall standard error of the electrostatic method was ± 47%, for a thorium lung burden of 0.22 Bq; while for the earlier scintillation method, the relative standard error of the measurement was ± 95%for a (^{228}Th) lung burden of the subject of 2.22 Bq ; only when the thorium (^{228}Th) lung burden reached 4.44 Bq did the measurement error drop to ±53%. This means that the sensitivity of the new method is higher than that established in 1979 by a factor of 20.

Table 6. Comparison between the present method and that of ANL.

	This method	ANL method
Background [counts/min]	0.003	0.005
Median variance coefficient of thoron activity outside the body	±17%	±15%
Total efficiency [%]	70	50
Minimum detection limit for exhaled thoron (Bq)(zero±2σ)	0.007	0.01
Lower limit for the detection of thorium contamination in the miner's lungs (Bq)[^{224}Ra at the mouth]	0.068*	0.074
Overall uncertainty in dependence on the value of the emanating ^{224}Ra at the subject's mouth	0.037-3.70Bq (±0.013-0.07 Bq)	0.037-3.70Bq (±0.011-0.74 Bq)
Measurement time [hours]	3.33+	30+
Manufacturing price [US $]	2000-3000	20000-30000

* This value obtained from the ^{224}Ra activity at the mouth of 10 unexposed people at the Bayun Obo Mine area.

Table 6 shows that, not only was the total efficiency of the new portable system higher than that of the ANL apparatus, but also all but one of the other parameters were somewhat better. Because the total measurement time of our system was much shorter than that of ANL, the overall standard error in measuring subject's ^{224}Ra emanation at a value of 0.037 Bq was somewhat higher than that of ANL. However, as a whole, the main parameters of our new method achieve similar levels to that of the ANL system, which is already known to have the sensitivity in the world for the measurement of exhaled thoron. In addition the minimum detection limit of thoron outside the body of our system is 0.007Bq, which is much lower than the 0.36Bq reported in 2005 by Sathybama, while the total counting time is much less than that of Sathybama et.al. (200 minutes vs 20 hours)[10].

4. Conclusions

In this paper, a portable system, using electrostatic collection, for the measurement of exhaled thoron activity in humans has been described. The basic theory, equipment, calibration process, measurement and the preliminary use are described. Based on the experience and the technology learnt from ANL, modifications were made to the equipment used, the collection conditions, measurement time and calculation procedures. The measurement time was shortened from 30 hours to 200 minutes, the negative high voltage raised from 5.8 kV (as used by ANL) to 9.0 kV; this raised the total efficiency from 50%(ANL) to 55% and the minimum detection limit decreased to 0.007 Bq(zero activity±2σ). The total standard error is 47%, for a thorium lung burden of 0.22 Bq, which is the detection limit recommended by ICRP Publication 10[11] for thorium lung burden using exhaled thoron activity measurements. The average background of the new scintillation detector was 0.003 counts/min.

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