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A Critique of the “EPA Method” for Analyzing and Calibrating Charcoal Canisters for Radon Measurements

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ABSTRACT

After the publication of *EERF Standard Operating Procedures for Rn-222 Measurement Using Charcoal Canisters* in 1987, an instrument manufacturer marketed an analysis system which contained the methodology and calibration factors utilized by the EPA radon laboratory in Montgomery, Alabama for measurement of radon in air using 4-inch charcoal canisters. The system also included a methodology for the analysis of the smaller charcoal canisters developed at the University of Pittsburgh. The use of this turnkey system for analyzing charcoal canisters has led to several problems and misunderstandings related to calibrating and analyzing charcoal canisters for the measurement of radon in air. This paper describes the “EPA method” for analysis of four-inch, open-faced charcoal canisters, problems with the method itself, problems due to misapplication of the method and an alternative to the method.

Introduction

In 1987 the Eastern Environmental Radiation Facility (EERF) of the U. S. Environmental Protection Agency (EPA) published a manual (Gray and Windham 1987) documenting its procedure for using four-inch open-faced charcoal canisters to measure indoor radon concentration. The original manual contained information for the calibration of charcoal canisters in a chamber where the air was relatively stagnant. Later an addendum was added to the manual containing calibration factors for canisters in an active air environment, which more closely resembles a residential indoor environment.

The manual describes a method of calibrating open-faced charcoal canisters, and their use for measuring ambient radon in indoor air, that has come to be called by some the “EPA method.” However, it was not intended that the method described in the manual be construed as a “standard” method, rather that the manual documented the method that was in use at the EERF. Although this paper criticizes method, the reader should in no way infer a criticism of how the method was applied at the EERF. Rather this paper is critical of how the method has been and is being applied, and sometimes misapplied, within the radon testing industry. Further, the reader should not infer criticism of charcoal canister analysis laboratories in the radon testing industry. The

author believes that where this method has been misapplied in the industry, the personnel involved were well intentioned but simply were not educated in the intricacies of the method or the software system that utilizes it. This paper is an attempt to correct this situation. The reader should also keep in mind that this paper relates specifically to four-inch open-faced charcoal canisters; although, the discussion presented here could possibly be applied to other configurations of charcoal detectors.

A Description of the Method

The EERF's approach is similar to that developed and reported by George (George 1984). The radon concentration in air is determined using the following equation:

$$C = \frac{R}{(T_s) (E) (CF) (DF)} \quad (1)$$

where C = Radon concentration (pCi/L)

R = Net count rate (counts per minute or cpm)

R = [Gross count rate (cpm)] - [Background (cpm) of the detector for that day]

T_s = Canister exposure time (min)

E = Detector counting efficiency (cpm/pCi)

CF = Calibration factor (L/min)

DF = Decay factor from the midpoint of the exposure to the beginning of count

$DF = \exp[-\lambda (T_D + T_s/2)]$

where λ = decay constant for ^{222}Rn (min^{-1})

$\lambda = \ln(2) / t_{1/2}$ [$t_{1/2}$ = half-life of ^{222}Rn (min)]

T_D = time from end of exposure to beginning of count (min)

The background count rate (cpm) and the detector efficiency (cpm/pCi) are determined each day that the system is used. The detector efficiency is determined by counting a standard canister containing ^{222}Rn in secular equilibrium with a known quantity of ^{226}Ra . In this author's opinion, the decay factor, DF , should be defined

differently, but as long as the above definition is used consistently during both calibration and analysis of samples, the DF as defined above works as well as other alternatives. This has been discussed in more detail elsewhere (Jenkins 1991).

The crux of this paper is the calibration factor, CF. Note that this factor has the unit of liters/minute (L/min), as if it were a flow rate. A reasonable analogy is that [(CF) x (T_s)] could be thought of as the volume of air from which radon is totally removed, as if air were pumped through a system that removed and trapped the radon. Some contend that the CF and T_s should be combined into a different calibration factor that has the unit of volume (Blue and Jarzempa, 1992). But, in this paper the CF remains as used by the EERF.

The CF for a given exposure of a charcoal canister is a function of the sampling time and the relative humidity of the air to which the canister is exposed. However, it should be made clear “up front” that the parameter that is measured and used in the calibration and analysis of charcoal canisters is not the relative humidity but rather the mass of moisture adsorbed during the exposure, which itself is a function of relative humidity. The relative humidity is not measured during a field exposure. Relative humidity is only a consideration because canisters must be exposed over a range of relative humidity values for calibration purposes.

In calibrating charcoal canisters, it is necessary to derive a family of calibration factors for various times of exposure and values of mass of adsorbed moisture. This is typically done by exposing groups of canisters in a controlled radon chamber for a minimum of three exposure periods covering the time periods that are used for field measurements and at three values of relative humidity; a low value between 20% and 30%, a medium value between 45% and 55% and a high value between 70% and 80%.

The EPA manual referenced above describes the calibration of four-inch open-faced charcoal canisters that were used “as received” from the manufacturer, without heating them to remove the moisture present in them at the time of manufacture. Each canister was used once and then discarded. Five canisters each were exposed in the radon chamber at the EERF for exposure times of 1, 2, 3, 4, 5 and 6 days and at relative humidity values of 20%, 50% and 80%. In all, ninety canisters were exposed for the calibration. The CF for each canister was calculated using the following equation:

$$CF = \frac{R}{(T_s) (E) (C) (DF)} \quad (2)$$

Please note that Equation (2) is merely Equation (1) rearranged to solve for CF instead of for C. The fifteen values of CF for the canisters exposed for two days are shown in Table 1. A plot of CF as a function of moisture gain for the two-day canisters contained in the EPA manual is reproduced here as Figure 1. This is assumed to be a curve of “best fit” to the data shown in Table 1.

According to the algorithm used by the EERF, the first step in determining a value of CF for a canister used for a field measurement is to select an “Initial CF” value, based on the observed mass of moisture gained during the exposure, from the curve shown in Figure 1. Although Figure 1 contains CF values only for exposure times of 48 h, this “Initial CF” is taken from this curve regardless of the actual exposure time. If the actual exposure time was 48 h, then this “Initial CF” value is the “Final CF” value used in Equation (1).

For exposure times other than 48 h, the algorithm uses a set of “Adjustment Factors” (AF) to adjust the “Initial CF” to a value that is appropriate for the actual exposure time. The AF values are shown in Table 2. These AF values are assumed to have been derived from the CF values determined by EERF for canisters exposed for periods of time other

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Table 1. Calibration Factors from EERF for two-day canisters in an active environment

Relative Humidity (%)	Mass of moisture gain (g)	CF (L/min)
20	0.0	0.125
20	0.0	0.125
20	0.0	0.126
20	0.0	0.120
20	0.0	0.126
50	1.0	0.120
50	1.0	0.130
50	1.0	0.120
50	1.0	0.121
50	1.0	0.121
80	7.6	0.089
80	7.9	0.096
80	7.5	0.090
80	7.4	0.089
80	7.6	0.094

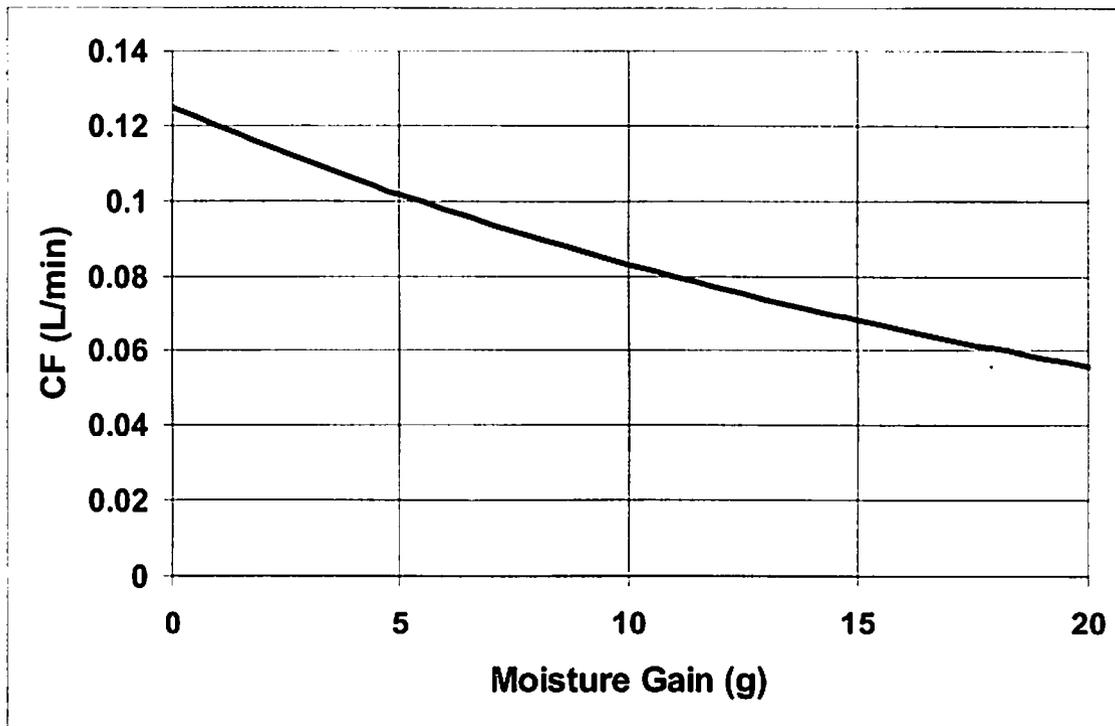


Figure 1. Calibration Factors [CF (L/min)] for a two-day exposure

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Table 2. Adjustment Factors (AF) from EERF

<u>Exposure Time (h)</u>	<u>20% RH AF (L/min)</u>	<u>50% RH AF (L/min)</u>	<u>80% RH AF (L/min)</u>
24	0.169	0.164	0.137
24	0.158	0.177	0.141
24	0.168	0.161	0.140
24	0.165	0.164	0.134
24	0.155	0.167	0.140
48	0.125	0.120	0.089
48	0.125	0.130	0.096
48	0.126	0.120	0.090
48	0.120	0.121	0.089
48	0.126	0.121	0.094
72	0.102	0.096	0.065
72	0.098	0.102	0.066
72	0.103	0.096	0.065
72	0.097	0.097	0.062
72	0.102	0.100	0.063
96	0.087	0.081	0.049
96	0.086	0.087	0.054
96	0.087	0.083	0.050
96	0.083	0.081	0.049
96	0.088	0.084	0.051
120	0.078	0.072	0.039
120	0.075	0.074	0.040
120	0.076	0.070	0.038
120	0.075	0.069	0.038
120	0.076	0.072	0.040
144	0.069	0.064	0.030
144	0.070	0.068	0.032
144	0.071	0.063	0.027
144	0.070	0.062	0.028
144	0.070	0.063	0.031

than 48 h, but this cannot be verified because EERF published CF values only for the 48-h canisters. Note that the AF values have the unit of L/min, just as the CF values do. EERF apparently chose to define the AF values for 48-h canisters to be identical to the CF values for 48-h canisters, as can be seen from Tables 1 and 2. Curves of the AF values are reproduced here as Figure 2. There is one curve each for the three values of relative humidity; 20%, 50% and 80%.

The algorithm provides a method for determining which of the curves of AF values to use, based on the mass of moisture the canister gained during the exposure. This method is summarized in Table 3. If the moisture gain was less than 1.0 g, then the 20% curve is used. If the moisture gain was between 1.0 and 4.0 g, then the 50% curve is used. If the moisture gain was greater than 4.0 g, then the 80% curve is used. Values of AF for the actual exposure time and also for an exposure time of 48 h are determined from the appropriate humidity curve. Then the following equation is used to calculate the final value of CF.

$$\text{Final CF} = \text{Initial CF} \times (\text{AF for actual exposure time}) / (\text{AF for 48 h exposure time}) \quad (3)$$

In other words, the ratio of the AF for the actual exposure time to the AF for a 48-h exposure time becomes a modifying factor by which the “Initial CF” is multiplied to produce the “Final CF.” This final value is then used in Equation (1) to determine the radon concentration during the exposure.

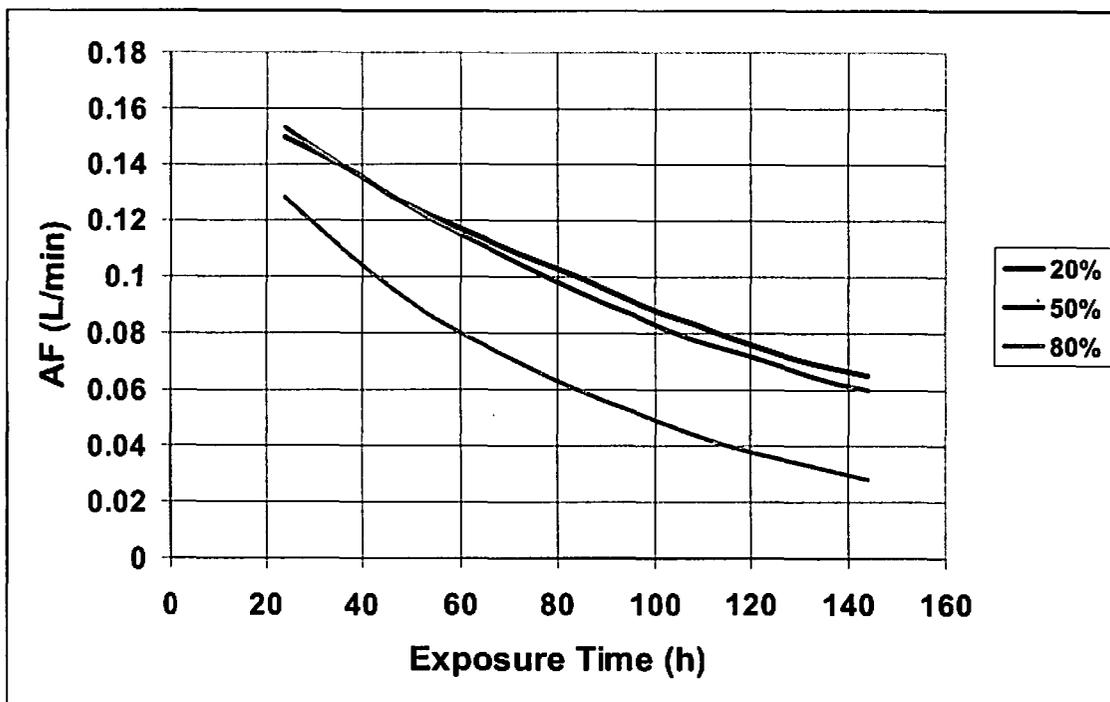


Figure 2. Adjustment Factors [AF (L/min)] for three values of relative humidity

Table 3. Selection of AF curve

<u>If mass of moisture gained is:</u>	<u>Then use curve for:</u>
< 1.0 g	20%
1.0 g to 4.0 g	50%
> 4.0 g	80%

Because it is the ratio of two Adjustment Factors that is used as a modifying factor to adjust the “Initial CF,” it can be seen that EERF’s choice to set the AF values for the 48-h canisters equal to the CF values for the 48-h canisters, and to give the AF values the unit of L/min, was an arbitrary choice. There is no physical meaning to the AF values’ having any unit at all, and they in fact probably should be unitless. Further, the AF values for the 48-h canisters could be set to any arbitrary value, as long as the AF values for the other exposure times are chosen so that the ratios are appropriate for converting “Initial CF” values to “Final CF” values.

With the prolific use of computers today, the concept of using graphs to determine calibration factors and adjustment factors seems cumbersome, antiquated and prone to errors. However, the method apparently worked well for the radon lab at the EERF.

The Problems

1. Use of EERF calibration data by other laboratories

After the EERF published its procedure and calibration data, a charcoal analysis system was marketed by a private manufacturer, which incorporated the “EPA method” and EERF’s calibration data into its analysis software for 4-inch open-faced canisters. Although the manufacturer no longer supports this turnkey system, several charcoal laboratories, often with little or no understanding of how the software works, are still using it.

There are several problems with using the turnkey system, but probably the largest one is that some laboratories used the system, and the built-in calibration factors from EERF, without any calibration of their own charcoal devices whatsoever. If the charcoal canisters used by the laboratory were exactly the same as those used by the EERF, and if they were used in exactly the same manner, then perhaps the EERF calibration factors would be appropriate. However, this should be verified constantly by obtaining and analyzing spiked samples, and this was often not done. Therefore, the turnkey software system made it too easy for laboratories to analyze charcoal canisters with a system that was not calibrated, or at least whose calibration was unverified, by the end user. This is obviously against EPA protocols; however, the protocols are not followed by everyone and are enforced by only a few states.

2. The method itself

Besides the obvious problems with determining calibration factors and adjustment factors from graphs, there appears to be a problem with the “EPA method” itself. There is no problem if the exposure time happens to be 48 hours. The problem is in the use of the “Adjustment Factors” to correct to an exposure time different from 48 hours.

From Figure 2, it is seen that there is not a large difference between the low humidity and medium humidity curves. So if the algorithm for selecting among the AF curves (Table 3) caused the low humidity curve to be used, when in reality the medium humidity curve should have been used, or vice versa, then the resulting error is probably not significant. However, the same cannot be said about the difference between the medium humidity curve and the high humidity curve in Figure 2. There appears to be a significant difference between the two curves, but it must be remembered that it is the ratio of the two AF values in Equation (3) that is important, not the actual AF values themselves. So, what is important to know is how this ratio, or modifying factor, changes as a function of the humidity to which the canister is exposed, and this cannot be easily discerned from Figure 2. The plot in Figure 3 shows this ratio of the AF values as a function of exposure time and relative humidity.

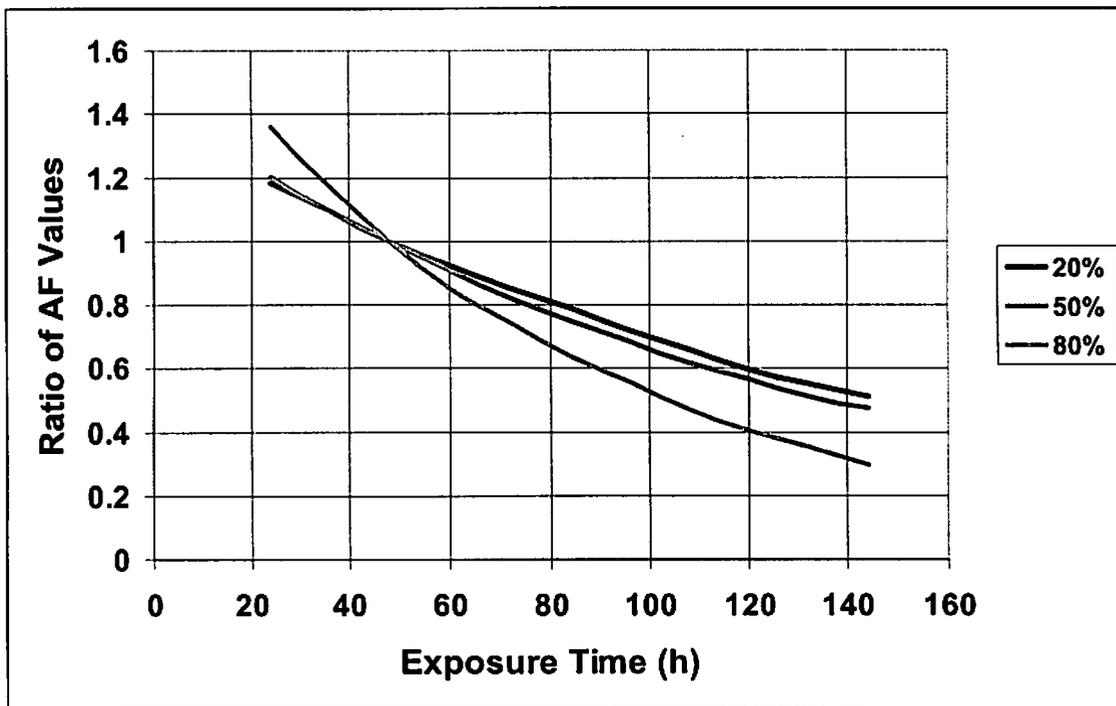


Figure 3. Ratio of Adjustment Factors for three values of relative humidity

From Figure 3 it is seen that the ratio of AF values, i.e. the modifying factor in Equation (3), is similar in value for the low and medium humidity curves regardless of the length of the exposure. However, the modifying

factors for the medium and high humidity curves are significantly different for exposure times much smaller or much larger than 48 hours. This is seen more clearly in Figure 4, which shows two curves; the ratio of the modifying factor for the medium humidity curve to that of the low humidity curve, and the ratio of the modifying factor for the high humidity curve to that of the medium humidity curve. It is easy to see from Figure 4 that the change in the modifying factor that occurs at the breakpoint of 1.0 g according to the EERF algorithm is fairly small regardless of the exposure time and approaches approximately 7% at an exposure time of 144 h. However, the change in the modifying factor that occurs at the breakpoint of 4.0 g can be significant, exceeding 10% for an exposure time of 72 h and 30% for an exposure time of 144 h. So, a canister for 72 h or longer could have a quite different calibration factor applied during the analysis, depending on whether the moisture gain was 4.0 g (or less) or 4.1 g (or more).

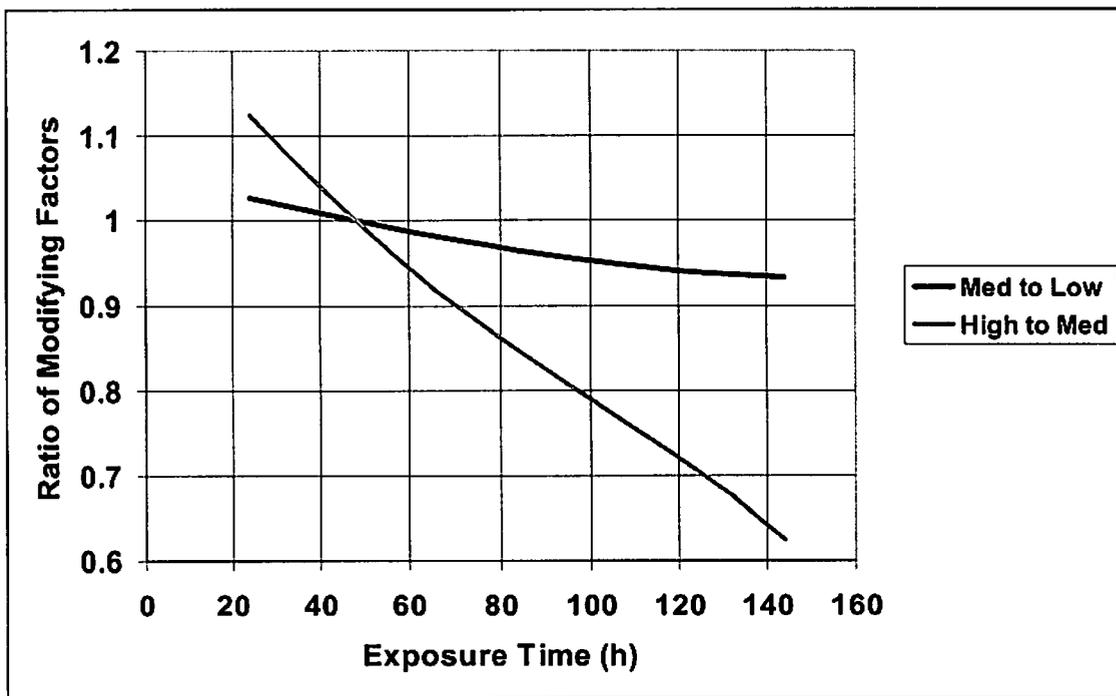


Figure 4. Ratio of Modifying Factors

3. Between the curves

What are the chances that the wrong curve in Figure 2 would be selected by the EERF algorithm? To judge that, one needs to know the mass of moisture gain for all of the canisters calibrated by EERF; however, EERF published only the moisture gains for the 48-h canisters as shown in Table 1. Blue and Jarzempa published values of moisture gain for all of the exposure times and for the type of canister used by EERF. It is not clear from their publication if these values actually came from EERF through a private communication, or whether Blue and Jarzempa exposed similar canisters in a controlled atmosphere for the needed time periods. Regardless, their published values are reproduced here as Table 4.

Table 4. Observed moisture gains for EERF canisters

<u>Exposure Time (h)</u>	<u>Observed Mass of Moisture Gain (g)</u>		
	<u>20%</u>	<u>50%</u>	<u>80%</u>
24	-0.4	0.7	4.5
48	-0.5	1.0	7.5
72	-0.5	1.2	10.5
96	-0.5	1.3	11.9
120	-0.5	1.4	13.4
144	-0.5	1.5	15.8

As seen in Table 4, the mass of moisture gain for the 20% relative humidity condition was for all exposure times slightly less than 0.0 g. This makes sense because the canisters were used “as received” from the manufacturer without heating them to remove any moisture that was present at the time of manufacture. The

values of mass of moisture gain published by the EERF, and shown in Table 1, probably should have been less than 0.0 g.

From Table 4, it is also seen that for the EERF canisters the algorithm for selecting the appropriate AF curve as outlined in Table 3 makes sense. In every case but one, the mass of moisture gain was less than 1.0 g for the exposures at 20% RH, between 1.0 and 4.0 g for exposures at 50% RH and greater than 4.0 g for exposures at 80% RH. However, field exposures are not carried out in atmospheres of controlled relative humidity. The relative humidity is likely not constant during the exposure of a field sample, and probably also is not measured. Therefore, the relative humidity values given throughout this paper have no meaning other than for the canisters that were used in the calibration procedure.

It is certainly conceivable that a canister similar to those used by the EERF could be exposed for 72 h or more to a relative humidity condition that, on the average, was somewhere between 50% and 80%, and yet the mass of moisture gain was 4.0 g or less. In this case, some AF value between the 50% and 80% curves might be appropriate, but the “EPA method” and the turnkey software has no choice but to default to the 50% curve. In which case an error is introduced that could be over 10%. It would be much more desirable to use an algorithm that was continuous with mass of moisture gain. In other words, an algorithm that would produce an appropriate value for AF or CF for any value of mass of moisture gain rather than having breakpoints at certain values. The “EPA method” and the turnkey software do not provide for selecting values between the curves, although they might be more appropriate.

4. Recycled canisters

Many charcoal laboratories recycle their charcoal canisters by heating them in an oven to remove any adsorbed moisture and radon before reusing them. This means first of all that the calibration data produced by EERF are

totally inappropriate for those charcoal canisters. In this case, the canisters do not start with a quantity of moisture in them, so the amount of moisture adsorbed during exposure should be greater than that observed for the EERF canisters. Therefore, it is essential that charcoal laboratories that recycle their canisters produce calibration factors for their own detectors, but this has not always been done.

Secondly, the EERF algorithm for selecting the appropriate AF curve, which is built into the turnkey software, is not appropriate for recycled canisters. The breakpoints used in the EERF algorithm are not appropriate for recycled canisters, but there is no way to change the algorithm in the turnkey software. Even canisters exposed at a condition of 50% relative humidity can adsorb more than 4.0 g of moisture when they start out with no moisture. So, even if a charcoal laboratory produces a set of calibration factors for their detectors, as long as the turnkey software is used, it would not always select the appropriate AF curve and significant errors could result. It is possible to modify the table of calibration factors and adjustment factors used by the software to adjust to more appropriate values for recycled canisters, but this still is not an ideal solution to the situation. No matter how this is done, significant errors in calculating the calibration factors to be applied to field samples can be made. The EERF algorithm does not distinguish between canisters that adsorb 4.1 g of moisture and 20 g of moisture; the same calibration factor would be used for both ends of this range. For recycled canisters exposed for 72 hours or more, this can be a significant source of error.

A Better Alternative

With the common use of computers today, there are much better approaches to the analysis of charcoal canisters than using methods that require looking up values from curves or tables. Further, algorithms that include adjustment factors and selections among set curves based on moisture gain should be avoided, particularly when they are not appropriate for the type of charcoal canister that is being used. Instead, a model or equation that

produces calibration factor values that are continuous with the parameters of exposure time and moisture gain can be developed to fit the calibration data. Such an equation can be used in spreadsheets, computer programs or even handheld calculators. This approach always results in the best value of CF, based on calibration data, for any given set of values of exposure time and moisture gain. The details of one goes about analyzing calibration data to produce a best fit according to a given model are beyond the scope of this paper; however, a few approaches are described here.

One approach is to use a linear regression model that is second- or third-order (or higher order) in the parameters of exposure time and mass of moisture gain to fit the calibration data. Again note that relative humidity does not enter into the model at all, and only is an issue because canisters must be exposed at different controlled values of relative humidity in order to produce calibration data. A possible third-order linear model looks like the following:

$$CF = b_0 + b_1 T + b_2 M + b_3 T^2 + b_4 M^2 + b_5 TM + b_6 T^3 + b_7 M^3 + b_8 T^2 M + b_9 T M^2 \quad (4)$$

where T = exposure time (d or h)

M = mass of moisture gain (g)

b₀ through b₉ = regression coefficients (constant values resulting from the regression analysis)

A “stepwise” regression procedure can be used to add terms to the model in order of improving the fit to the calibration data until some criteria is met that causes no more terms to be added to the model. The likely result of such a procedure is that not all of the terms shown in Equation (4), or some similar linear model, would remain in the model. In other words, the regression coefficients for one or more terms would not be significantly different from zero and therefore those terms would not remain in the model. A good fit to the calibration data is possible with this type of model; however, one must be careful not to extrapolate at all

outside the range of the calibration data as the values of CF that might result could be totally inappropriate.

This type of model and its limitations are discussed elsewhere (Jenkins 1991).

Blue and Jarzempa proposed a model that is based on the physical process of adsorption of radon onto charcoal.

This model is nonlinear in the parameters of exposure time and moisture gain. Their model is as follows:

$$CF = \alpha [1 - \exp(-\delta t)] - \beta [1 - \exp(-\delta t)] M \quad (5)$$

Where t = exposure time

M = moisture gain

α , β and δ are constants based on physical properties of charcoal

Note that this model has a sound physical basis in that the coefficients all have some physical meaning based on the properties of the charcoal canister. For more details see Blue and Jarzempa, 1992. Blue and Jarzempa demonstrated that this model fits the EERF calibration data very well.

The model in Equation (5) was tried by this author at Bowser-Morner, Inc. in the early 1990's and was not found to be work well for recycled canisters. After some trial and error, a variation on this model was found to be more satisfactory. This model, which has been used successfully for about 10 years for recycled canisters, is as follows:

$$CF = b_0 \exp(b_1 T) \exp\{b_2 M [1 - \exp(b_3 T)]\} \quad (6)$$

Where T = exposure time (d)

M = moisture gain (g)

b_0 through b_3 are regression coefficients

Note that this model does not have a sound physical basis because the regression coefficients do not necessarily have any meaning related to the physical characteristics of the charcoal canisters, but rather are merely regression coefficients; i.e., values that produce the best fit to the calibration data.

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Figure 5 shows graphically a set of calibration data for recycled charcoal canisters exposed in the Bowser-Morner radon chamber at three relative humidity conditions and for periods of 2, 3, 4, 5 and 6 days (used by permission, please see acknowledgement below). Each data point on the graph represents the calibration factor for an individual charcoal canister, calculated using Equation (2). The curves are the lines of best fit for the entire family of data points taken as a group, using Equation (6) as the model. Although each individual curve shown in Figure 5 may not seem to be the best fit for the data for that particular exposure period, the family of curves taken as a whole is the best fit to the entire group of calibration data.

Please note that the scale on the Y-axis of the graph in Figure 5 was intentionally left blank. Further, the regression coefficients for the equation of best fit to these data are not reported here. These measures first of all provide some protection of the data on behalf of the client who paid for the calibration exposures in the first place, and secondly prevent the misapplication of the data by others as was done with the EERF calibration data.

The equation of best fit is Equation (6) with the proper values for the regression coefficients that resulted from a nonlinear regression procedure. This equation can be used in a spreadsheet or computer program to produce the best value, based on the calibration data, for the calibration factor for a charcoal canister for any value of exposure time and mass of moisture gain, without any approximations.

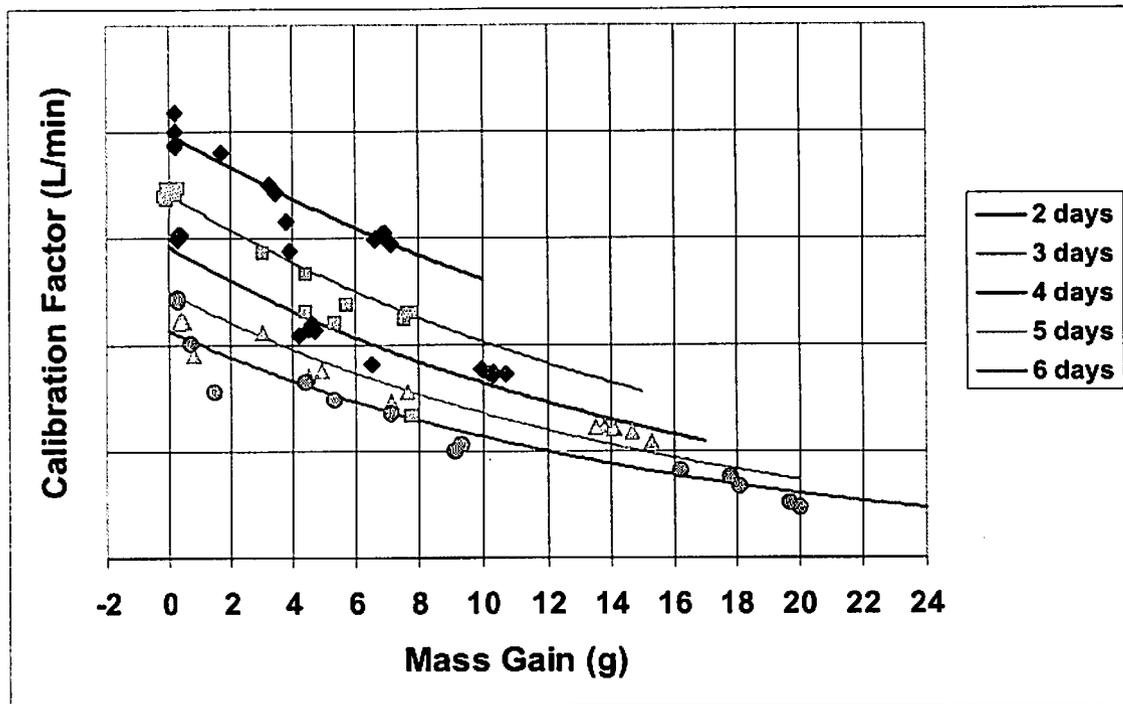


Figure 5. Calibration curves for recycled canisters using a nonlinear model

It can be easily seen from the clusters of data points in Figure 5 that most of the canisters that were exposed to a relative humidity of approximately 50% had moisture gains exceeding 4.0 g. So, clearly the breakpoint at 4.0 g used by the EERF algorithm and by the turnkey software is not appropriate for these charcoal canisters.

Conclusion

This author highly recommends that the turnkey software based on the EERF algorithm no longer be used by charcoal analysis laboratories. Instead, a method based solely on an equation of best fit to the laboratory's calibration data should be used.

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