FUEL RESEARCH INSTITUTE OF SOUTH AFRICA.

TECHNICAL MEMORANDUM NO. 13 OF 1954.

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On receipt of a query as to the accuracy of the Institute's calorific values, the position in regard to calorific values was investigated. A study of data on railway and export coals, which are regularly sampled and analysed, showed that there appeared to have been a slight decrease in dry ash-free calorific values as from about the beginning of 1953, with a tendency for the 1952 values also to be slightly low. Thus the average values of 23 railway coals for the years 1950 to 1953 were as follows :-

TABLE 1.

Average Annual Data.	1950	1951	1952	1953
Calorific Value (D.M.M.F.) lb./lb.	15.35	15.33	15.30	15.24
Ash %	13.85	13.90	14.14	14.36
Moisture %	1.96	1.96	1.94	1.72

The fall in moisture content in 1953 also appeared to be significant. It has never been the practice at the Institute to determine moisture contents simultaneously with calorific values, so the calorific values for 1952 and 1953 were calculated assuming 1.96 % moisture, giving values of 15.31 and 15.28 lb./lb. These differences are still significant.

The possible/.......

The possible effects of moisture variation were then considered. The calorific value room has been controlled for temperature and humidity since the latter part of 1951, although some considerable time elapsed before the plant was in proper working order, especially as regards the humidity control. For some considerable time the humidity of the room has been set at about 55 % humidity, and the temperature at about 24°C. Fifty five per cent humidity was chosen as this value was recommended by the Weather Bureau as being normal for Pretoria. In view, however, of the fact that the calorific value of coal is dependent on the moisture content ruling at the time of the calorific value determination, it was decided to ascertain the moisture contents of a series of railway coal samples in the calorific value room. In Table 2 below are given the results obtained together with results obtained after reducing the ambient humidity to 42 %, and the average moisture contents for the years 1950, 1951 and 1952, which latter all refer to coal in equilibrium with normal air conditions ruling in Pretoria.

TABLE 2.
MOISTURE CONTENTS OF RAILWAY COAL SAMPLES.

Colliery.	Average Data (Air Dry)			Samples at ± 55 % Humidity.	Samples at ± 42 % Humidity.
	1950	1951	1952		
Douglas	2.0	2.0	2.0	2.5	2.2
Springbok	2.2	2.2	2.1	2.5	2.25
Union	2.6	2.6	2.6	3.0	2.9
Marsfield	2.4	2.4	2.4	3.0	2.75
Koornfontein	-	-	-	2.7	2.55
Phoenix	2.3	2.3	2.2	2.7	2.5
Van Dyksdrift	2.1	2.2	2.1	2.6	2.4
Tweefontein	2.2	2.2	2.1	2.3	2.3
Greenside	1.9	1.9	1.8	2.2	2.0
Durban Navigation	1.4	1.5	1.4	1.7	1.55
Cambrian	1.4	1.3	1.3	1.6	1.35
Hlobane	1.4	1.2	1.2	1.4	1.25
Burnside	0.9	0.9	1.0	1.1	0.9
Tshoba	1.2	1.5	1.2	1.5	1.25
Coronation	2.3	2.2	2.3	-	2.5
Wolvekrans	2.0	1.9	2.1	-	2.25
New Schoongezicht	-	-	-	-	2.6

From Table 2 it is obvious that the humidity setting of 55 % gives much higher moisture contents than the average values ruling for the period 1950 to 1952. Even with the setting at 42 % humidity, the results tend to be rather high, although the Natal coals agree fairly well with the normal air dry moistures.

If the high moisture contents shown in Table 2 for the 55 % humidity setting have applied to coals over the past 18 months or so, the reduced values obtained for calorific values can be accounted for. Thus the average difference in moisture content of the thirteen coals on which comparative data are available is 0.325 %, equivalent to a difference in dry mineral matter free calorific value of 0.05 lb./lb. This is equivalent to bringing the D.M.M.F. calorific value for 1953 (Table 2) up to about 15.33 lb./lb., which is very similar to the 1950/1951 values. It seems thus that the whole cause of the inaccuracy of the calorific values of the past 18 months was the high moisture content ruling in the calorific value room. (The moisture contents of the coals were determined on the samples in the normal air dry condition). In order to keep a check on the moisture contents of coal in the calorific value room, it has been adopted as standard practice that proximate analysis on export grading samples be done weekly and on railway coals be done monthly, the samples being in equilibrium with the air conditioned atmosphere ruling in the calorific value room and the balance room adjoining. If moisture contents differ appreciably from the 1950/1952 averages, the humidity shall be adjusted accordingly.

In order to test the agreement in calorific values between the Fuel Research Institute, Douglas Colliery and the Transvaal Coal Owners Association, two sets of samples of

six coals/.........

six coals were prepared and duplicate calorific value determinations done on them. The moisture contents were determined on these samples at the same time as the calorific values. One series of samples, together with a sample of paraffin oil (medicinal liquid paraffin) were sent to both Douglas Colliery and the Transvaal Coal Owners Association for similar analyses. The Transvaal Coal Owners Association subsequently sent their series of samples on to the Goldfields Laboratory. The results obtained together with calorific values calculated to the dry basis are given in Table 3. (See overleaf).

Comparing the dry calorific values, the average data are (1) 12.87 (2) 12.90 (3) 12.97 lb./lb. and (4) 12.83 and (5) 12.97 lb./lb. The T.C.O.A. and F.R.I. results agree well together and this agreement is borne out by the similarity of the values obtained for the paraffin oil. The Goldfields and Douglas results are both higher, and by about the same amount, and this similarity is borne out by the similarity of the values obtained for the paraffin oil. There is some variation between the differences obtained on individual samples, but this can at least partly be ascribed to the fact that the outside laboratories do not have air conditioning, and it is well known that values tend to vary with the time of day due to changes in air temperature. Normal experimental errors would probably account for the remainder of the variation in the differences obtained for individual samples.

It appears that the results obtained by the Goldfields Laboratory and by Douglas Colliery are too high. This is borne out by the high values obtained for the paraffin oil, which has been used for at least five years at the Institute as a test substance, and has always given values very close to 20.40 lb./lb. This value is in very good agreement with the

Merck's/..........

TABLE 3.

COMPARATIVE CALORIFIC VALUES AT DIFFERENT LABORATORIES.

| | (a) Samples sent to T.C.O.A. | | | | | | | | | (b) Samples sent to Douglas Colliery. | | | | | |
| | (1) F.R.I. Analyses. | | | (2) T.C.O.A. Analyses. | | | (3) Goldfields Analyses. | | | (4) F.R.I. Analyses. | | | (5) Douglas Analyses. | | |
Sample	C.V. lb./lb.	H_2O %	Dry C.V. lb./lb.	C.V. lb./lb.	H_2O %	Dry C.V. lb./lb.	C.V. lb./lb.	H_2O %	Dry C.V. lb./lb.	C.V. lb./lb.	H_2O %	Dry C.V. lb./lb.	C.V. lb./lb.	H_2O %	Dry C.V. lb./lb.
1.	12.32	2.5	12.64	12.36	2.6	12.69	12.42	2.1	12.69	12.26	2.8	12.61	12.39	2.6	12.72
2.	12.87	1.9	13.12	12.89	1.9	13.14	13.00	1.5	13.20	12.87	1.9	13.12	12.93	1.7	13.15
3.	12.84	2.3	13.14	12.85	2.5	13.18	13.05	2.1	13.33	12.75	2.5	13.08	12.88	2.5	13.21
4.	12.52	2.3	12.81	12.52	2.4	12.83	12.67	1.8	12.90	12.43	2.6	12.76	12.64	2.3	12.94
5.	12.08	2.4	12.38	12.08	2.4	12.38	12.21	1.9	12.45	11.97	2.7	12.30	12.20	2.4	12.50
6.	12.87	1.8	13.11	12.93	1.9	13.18	13.04	1.5	13.24	12.84	2.1	13.12	13.06	1.9	13.31
Oil.	20.39	-	-	20.37	-	-	20.70	-	-	20.39	-	-	20.67	-	-

Merck's thermochemical standard liquid paraffin used by the Institute for standardisation (benzoic acid is actually generally used) which has a calorific value of 10990 cal./gm., equivalent to 20.390 lb./lb.

Although it appears that the moisture content of the coal was all that was at fault, it was decided to investigate the methods of calorific value determination in use at the Institute, and if possible to abide by the recommendations of the South African Standard specification[1]. The bombs used at the Institute are of the Scholes type, and are rather heavy, and some difficulty has been experienced with getting good check values, mainly due to the long chief periods of the apparatus. For this reason, the Institute has in the past diverged from standard practice in that the calorimeter has been at the same, or even at a slightly higher, temperature than that of the jacket. At the Institute the jacket consists of a 6 ft. diameter water bath thermostatically controlled at 25.0 $^{\circ}$C. It was decided to return to standard practice in this respect, and make the maximum calorimeter temperature 24.5 $^{\circ}$C, so that the calorimeter was not less than 0.5 $^{\circ}$C below the jacket temperature. The method of operation is described in detail in the F.R.I. Report No. 21 of 1950 by S.D. Coetzee.

Various tests were carried out under these circumstances with the three bombs in use. However, it was found that there was a tendency for a maximum temperature to occur which was maintained for a period of 3 to 4 minutes before the temperature began to fall. This increased the chief period - in all this work the chief period is defined as the period in minutes from firing to the minute reading after which a constant fall is obtained, and not from firing to the first minute reading after attaining the maximum as specified in S.A.S.I. No. 5 of 1940 - and good agreement of duplicates was not always possible.

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This applied particularly to one bomb, but it was found that
two of the bombs definitely gave better results when the differ-
ence between the calorimeter and the jacket was a maximum of
0.5 °C instead of a minimum of 0.5 °C and the conditions were
changed accordingly. The results given below refer only to two
bombs, one of which (bomb A) was maintained throughout at an
initial temperature difference of at least 0.5 °C.

The water equivalents and calorific values were
determined according to two formulae as follows:-

Formula 1 : $T = t_x + mf - (f + i)$

Formula 2 : $T = t_x + mf - (f + i) F$ where

$$F = m - \frac{1}{t_x} \left(\sum_{1}^{m-1} (t-t_o) + \frac{t_x}{2} \right)$$

T = Corrected rise in temperature.

t_x = Uncorrected rise in temperature, that is $t_m - t_o$.

t_o = Temperature of calorimeter at firing.

t_m = The last reading of the chief period. (This is the
first temperature reading after which the rate
of fall is constant).

m = Number of minutes in the chief period.

i = The rate of rise of temperature per minute in the
initial period.

f = The rate of fall of temperature per minute in the
final period.

Formula 1 is essentially the formula of S.A.S.I. No.
5 of 1940, the only divergence being the definition of m, which
has already been explained. Formula 2 is the formula of Schultes
and Nübel in a different form, and is essentially similar to
the Regnault Pfaundler equation. It has been used in preference
to the latter due to the simpler calculations involved.

The reader is referred to "Calorimetry" by F.W. Quass[2] for
comparative results using these two formulae.

The bombs were standardised with benzoic acid using
a temperature difference of at least 0.5 $^{\circ}$C. The water equivalents
obtained were the same as had been obtained using the conditions
previously ruling. The results are given in Table 4.

TABLE 4.

DETERMINATIONS OF WATER EQUIVALENTS.

| Bomb | m | f | i | t_x | Correction. | | F | Water Equivalent. | |
					Formula 1	Formula 2		Formula 1	Formula 2
A	6	0.0038	0.002	2.000	0.017	0.0182	0.794	3496	3494
A	8	0.0042	0.002	1.948	0.0274	0.0285	0.826	3492	3490
A	7	0.0036	0.002	1.997	0.0196	0.0210	0.744	3487	3484
A	7	0.0036	0.0025	2.040	0.0191	0.0207	0.737	3499	3496
B	7	0.0016	0.003	2.028	0.0066	0.0077	0.772	3460	3459
B	8	0.002	0.003	1.989	0.011	0.0124	0.721	3460	3458
B	7	0.002	0.0028	1.990	0.0092	0.0103	0.763	3471	3469
.B	6	0.0018	0.0028	2.013	0.0062	0.0075	0.720	3472	3470

The results of the determination of calorific values on various
samples of coal are given in Table 5, at the end of the report.

The data in Table 5 show that what differences exist
between the calorific values as determined by the two formulae
are small. In only one case, namely sample A 9874, did formula 2
give a higher result, and only once was formula 1 higher by as
much as 0.03 lb./lb., namely for sample 3979, bomb A. The results
above the line refer to anthracitic coals with about 10 % volatile
matter, and on these samples the differences are generally
larger than for the mainly high volatile bituminous coals below
the line. This may be ascribed to the high values of F obtained
for the anthracites. For the bituminous coals the differences
between the calorific values obtained by the two formulae are

higher/..........

higher by 0.01 lb./lb. for bomb A than for bomb B. There are two reasons for this; firstly, bomb A generally gives higher values of F, and secondly, the water equivalent of bomb A was taken as 3494 gms. instead of 3493.5 gm., this difference accentuating the differences of the results by the two formulae. It may be remarked that the negative difference for sample A 9874 is associated with the lowest value of F obtained, even including standardisation (Table 4) whereas the difference of 0.03 lb./lb. for sample 3979 was associated with the highest value of F; as the determination was conducted in bomb A, the difference is accentuated by the use of the incorrect water equivalent, as pointed out above. (The real difference between these results is 0.023 lb./lb., and not 0.03 lb./lb.).

The values of F generally lie between 0.7 and 1.3, and the coals in Table 5 include most of the types found in South Africa, so that values outside these limits are not often to be expected. Thus it appears that the formula 1, as used in this report, gives reasonable results for coals. It is possible that for cokes, where the factor can be expected to exceed 1.3 by a considerable amount, formula 1 will give results that will definitely be high.

The corrections for bomb A are larger than those for bomb B, due to the former generally having a lower value for i and a higher value for f. The cooling constants, defined as $\frac{f + i}{t_x}$, for the data given in Table 4 averaged 0.0027° per minute per degree for bomb A and 0.0025° per minute per degree for bomb B.

Since concluding the above investigation it was decided to replace the calorimeter vessel by stainless steel. At the same time the diameter of the vessel was reduced to a minimum consistent with free movement of the direct type stirrer, and the outer container - of copper - reduced in diameter to

give about half an inch clearance. When the new stainless steel
constant temperature bath is brought into service, it is the
intention to make the outer container also from stainless steel,
as it retains its polished surface with little attention.

In Table 6 are given the results of a randomly selected
series of duplicate determinations done in bombs A and B with the
stainless steel calorimeters during August 1954. In these de-
terminations the temperature readings during the first 3 or 4
minutes after firing were not taken so that only formula 1 could
be applied, and F could obviously not be calculated.

TABLE 6.

CALORIFIC VALUES WITH STAINLESS STEEL CALORIMETERS.

Sample No.	Bomb	m	i	f	t_x	c	Calorific Value lb./lb.
1	A	7	.0000	.0048	2.033	.0288	12.67
	B	6	.0014	.0036	2.066	.0166	12.68
2	A	7	.0010	.0050	1.960	.0290	12.23
	B	6	.0020	.0036	1.999	.0160	12.27
3	A	7	.0002	.0052	2.064	.0310	12.88
	B	6	.0022	.0038	2.095	.0168	12.86
4	A	7	.0020	.0050	2.014	.0280	12.55
	B	6	.0024	.0034	2.051	.0146	12.58
5	A	7	.0014	.0056	2.086	.0310	13.01
	B	7	.0028	.0028	2.129	.0140	13.05
6	A	7	.0018	.0052	2.069	.0294	12.89
	B	7	.0038	.0026	2.109	.0106	12.91
7	A	7	.0020	.0046	2.079	.0256	12.94
	B	6	.0036	.0026	2.118	.0094	12.95
8	A	8	.0040	.0014	1.745	.0058	10.76
	B	8	.0036	.0010	1.761	.0034	10.74
9	A	9	.0028	.0040	2.081	.0292	12.97
	B	6	.0022	.0034	2.118	.0148	12.99
10	A	7	.0012	.0052	2.145	.0300	13.37
	B	7	.0022	.0032	2.176	.0170	13.35

TABLE 6 (CONTD.)

Sample No.	Bomb	m	i	f	t_x	c	Calorific Value lb./lb.
11	A	7	.0024	.0048	2.052	.0264	12.78
	B	6	.0032	.0030	2.086	.0118	12.77
12	A	7	.0024	.0032	2.092	.0168	12.96
	B	7	.0036	.0028	2.116	.0132	12.96
13	A	7	.0014	.0038	1.898	.0214	11.80
	B	7	.0018	.0024	1.934	.0126	11.85
14	A	7	.0020	.0036	1.857	.0196	11.54
	B	7	.0029	.0026	1.885	.0132	11.56
15	A	7	.0026	.0034	1.940	.0178	12.03
	B	7	.0030	.0026	1.965	.0126	12.04
16	A	8	.0024	.0026	1.709	.0132	10.59
	B	7	.0026	.0012	1.735	.0046	10.59
17	A	8	.0020	.0032	1.780	.0204	11.07
	B	7	.0028	.0020	1.801	.0092	11.02
18	A	6	.0020	.0038	1.905	.0218	11.84
	B	6	.0026	.0026	1.935	.0104	11.85
19	A	8	.0020	.0038	1.880	.0208	11.68
	B	7	.0020	.0026	1.907	.0136	11.69
20	A	7	.0020	.0052	2.322	.0292	14.45
	B	7	.0026	.0032	2.362	.0166	14.48

From Table 6 it is apparent that the initial rate of rise is less for bomb A than for bomb B, the average values being 0.0019 °C and 0.0026 °C, while the reverse is the case with the final rate of fall, average values being 0.0042 °C and 0.0028 °C. The cooling constants, at 0.0030 °C and 0.0027 °C for bomb A and B respectively, are slightly higher than before the alterations were made, as are also the average corrections to the temperature rise at 0.0238 °C and 0.0126 °C for bomb A and B respectively.