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Technical Evaluation: Analysis of Chlorine in Coal by Oxidative Hydrolysis Microcoulometry

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Analysis of Chlorine in Coal by Oxidative Hydrolysis Microcoulometry

Technical Evaluation, September 2000

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ABSTRACT

In September 2000, EPRI published the results of a round robin laboratory study of analytical methods for mercury and chlorine in coal, Report Number 1000287. The round robin study demonstrated that none of the routinely used industry methods could consistently produce quantitative results below 200 parts per million (ppm) chlorine. Given that more than a third of U.S. coals have less than 200 ppm chlorine, the need for improved chlorine analysis methods was apparent. During the course of the EPRI study, a new analytical method for chlorine in coal was identified, which is based on oxidative hydrolysis microcoulometry. To evaluate this method, samples of seven U.S. thermal coals were submitted to five laboratories for chlorine analysis. The new method produced rapid and reliable results down to 10 ppm chlorine. This technical evaluation report compares the performance of the oxidative hydrolysis microcoulometry procedure with that of other commonly used methods for analysis of chlorine in coal.

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BACKGROUND

In September 2000, EPRI published the results of a round robin laboratory study, Evaluation of Methods for Analysis of Mercury and Chlorine in Coal [1000287]. In this study, 40 laboratories analyzed homogenous samples of U.S. thermal coals using a range of analytical methods. The round robin study demonstrated that none of the routinely used industry methods for chlorine in coal could consistently produce quantitative results below 200 parts per million (ppm). Given that more than a third of U.S. coals have less than 200 ppm chlorine, the need for improved chlorine analysis methods was apparent.

During the round robin study, the study coordinator, Quality Assurance International (QAI), learned of a new procedure for chlorine analysis of coal, oxidative hydrolysis microcoulometry. Based on successful results applying this technique to a well characterized coal sample, EPRI decided to evaluate the new method using seven of the coals employed in the round robin study. This would allow direct comparison of the new method with the chlorine methods evaluated in the round robin study.

1.1 Limitations of Existing Routine Methods for Chlorine

A wide range of analytical methods is currently used for analysis of chlorine in coal. In the EPRI round robin study, the methods used most frequently by the participating labs, and that received detailed evaluation in the study, were:

- ASTM D 2361 Bomb Combustion Potentiometric Titration
- ASTM D 4208 Bomb Combustion Ion Selective Electrode
- Bomb Combustion Ion Chromatography
- Eschka Ignition Ion Chromatography

All of the above are approved or are currently under development by the American Society of Testing and Materials (ASTM). These methods involve igniting coal in a stainless steel bomb in an oxygen atmosphere or in Eschka Mixture in a muffle furnace. A solution is added to the bomb or ignition crucible to absorb the chlorine compounds generated during the ignition process. The absorbing solution is treated to convert chlorine compounds to chloride in solution. The chloride can be detected using an ion selective electrode or an ion chromatograph.

In bomb combustion, the sensitivity of the method is constrained by the maximum weight of coal that can be burned in the combustion bomb, about 1.3 grams. The lower quantitative limits of the bomb combustion methods ranged from 200 to 300 µg/g (equivalent to parts per million) in the round robin study.

Coals that do not burn well can be a real problem for the bomb combustion method: these include high moisture or high ash coals, and at the other end of the spectrum, highly swelling coals that can be ejected from the sample crucible during the combustion process. Some practitioners resort to the use of combustion aids or mediators to deal with ashes and difficult to burn coals, but these substances can introduce significant opportunities for contamination. The large internal volume and surface of the oxygen bomb, as well as the number of contact surfaces and valves, increase the risk of contamination or incomplete recovery of chlorine. Chlorine can also be trapped in the bomb or crucible alloy, resulting in either low or erratic recoveries.

In addition to the complications discussed above, the bomb combustion procedure is not readily amenable to batch processing and analysis time for a single sample can be in the order of thirty minutes.

The Eschka preparation technique can produce low and erratic recoveries if chlorine is lost during the ignition process. Eschka mixture is an alkaline flux made up of sodium carbonate and magnesium oxide. The mixture can contract from the sides of the ignition crucible during the heating stage, allowing chlorine to escape. Covering the ignition crucibles can resolve the problem. In addition, Eschka mixture attacks the glazing on porcelain crucibles, which results in reduced or erratic recoveries of chlorine.

From a detection standpoint, the most significant limitation of the Eschka Ignition technique concerns the presence of inorganic ions in the Eschka mixture that can severely interfere with the determination of chloride. These ions must be suppressed in order to minimize the interference. The lower quantitative limit of the Eschka Ignition procedure in the round robin study was 300 µg/g.

Although the Eschka ignition procedure is readily amenable to batch processing, analysis time for a single batch is of the order of 1 day.

1.2 Limitations of Alternative Industry Methods for Chlorine

In addition to the methods that were evaluated rigorously in EPRI’s round robin study, several alternative methods are available for chlorine analysis. The two most commonly used alternate methods for chlorine in coal are X-ray Fluorescence (XRF) and Instrumental Neutron Activation Analysis (INAA)

XRF analyzers are relatively common in the commercial laboratory industry. An XRF determination requires some physical treatment but little or no chemical treatment of the coal sample. The test sample is irradiated with electromagnetic radiation or a particle beam. Electrons are expelled from the inner electron shells of the chlorine atoms present in the sample. Electrons from shells further out fill the vacancies, resulting in the release of X-ray photons. The number of photons released is proportional to the number of chlorine atoms in the sample.

Since the coal sample requires little or no dilution, XRF can quantitatively measure chlorine down to approximately 30 µg/g. Significant limitations associated with chlorine analysis by XRF are physical interferences related to particle size as well as spectral interferences primarily from sulfur, which is present in all coals. The particle size interferences can be minimized by adequate grinding and by pelletizing the sample under pressure. The spectral interferences can be resolved by design of the detection system.

The analysis times for chlorine are extremely rapid, on the order of less than a minute per sample. The equipment for XRF analysis is significantly more costly than that used in ASTM methods.

INAA is considered a reference analytical method for chlorine, and is often used in preparation of standard reference materials. However INAA is not commonly used in the commercial laboratory industry as it requires the use of nuclear radiation. It is normally employed by certifying agencies and research organizations.

In INAA, the coal sample is irradiated with neutrons. Chlorine atoms in the sample absorb neutrons to form radioactive isotopes. By monitoring the decay of the radioactive isotopes, it is possible to determine the amount of chlorine present. As a nuclear analysis, technique INAA is not subject to the chemical interferences inherent to spectroscopic methods. Since the coal sample requires little or no dilution, INAA can quantitatively measure chlorine down to approximately 10 µg/g. Analysis times are of the order of 1 day.

1.3 Overview of the Oxidative Hydrolysis Microcoulometry Method

Quality Associates International was contacted by COSA Instruments of Norwood, New Jersey to provide coal samples to help develop a procedure for the determination of chlorine in coal by oxidative hydrolysis microcoulometry.

The method is a modification of ASTM D 5808 "Determining Organic Chloride in Aromatic Hydrocarbons and Related Chemicals by Microcoulometry". The instrument used for this method is a modified Mitsubishi TOX-100 Total Organic Halogen (TOX) analyzer, which is normally used for analyzing organic halogens in liquid samples.

The procedure for TOX analysis involves injecting a liquid specimen into a combustion tube maintained at 900 ^{o}C. A flowing stream of 50% oxygen and 50% argon is passed over the sample. The chlorine in the sample is converted to hydrogen chloride (HCl). The HCl flows into a titration cell where it reacts with silver ions present in an electrolyte solution. The silver ions consumed are coulometrically replaced and the electrical work required to replace the silver ions is thus a measure of chlorine.

Since coal contains both mineral and organic chlorine and limited amounts of hydrogen compared to most organic halides the following modifications to the procedure were made:

- The coal sample is weighed into a quartz boat. The boat is inserted into a quartz tube, which extends into the combustion zone. An automatic drive, which has variable stops, such that it can be stopped at various points, is used to push the sample into the combustion zone.

- The oxygen stream used to combust the sample is bubbled through a water tower to saturate it with water vapor, thereby increasing the amount of hydrogen available for the production of HCl. A mg quantity of tungsten metal is mixed with the coal to achieve the temperatures required to promote release of mineral chlorine. The addition of tungsten can increase the temperature in the reaction zone to well in excess of 1500 ^{o}C.

- A series of scrubbers is placed after the combustion train to remove excess water and sulfur oxides.

The analysis time for a single sample is approximately 10 minutes. Analysis is normally carried out on 20 mg of coal although the weight can be readily lowered or increased to accommodate coals with high or low chlorine content, respectively. An autosampler is commercially available for the instrument.

Halides other than chlorine can potentially act as interferences in the oxidative hydrolysis microcoulometry method. Fluorine, which normally occurs in the range of 20 to 200 µg/g in coal, produces a low response in the detector, and thus does not interfere with the determination. Bromine and iodine, if present, are determined as chlorine. However, bromine usually does not exceed 2% of the chlorine present in coal while iodine rarely exceeds 0.2% of the chlorine present.

As an initial test of the method, samples of well-characterized coal from an international proficiency test organization, CANSPECS, were provided to one commercial laboratory and to the instrument vendor. The results of analysis were in excellent agreement with XRF and INAA results for the samples and both the within and between laboratory precision were superior to that produced by ASTM standard methods. Based on these results, EPRI decided to proceed with an evaluation of the method using the U.S. thermal coals examined in Phase 2 of the EPRI round robin study.

2

STUDY DESIGN AND METHODOLOGY

The study was carried out by Quality Associates International Ltd. of Canada (QAI), under EPRI sponsorship. QAI designed the study protocol, and performed the data review and statistical analysis. To permit an objective comparison of the oxidative hydrolysis microcoulometry method with the most commonly used standard methods, the study was carried out on the coals from Phase 2 of the EPRI round robin study.

2.1 Study Samples

This section describes the source, type, and chemical composition of each of the samples used in the study. The seven coals listed in Table 2-2 were used in this study. Certified values are shown in shaded boxes, reference values in italics and consensus values reported in EPRI report 1000287 in normal type. The EPRI coals represent a major proportion of U.S. thermal production. A certified reference material (CRM), NIST 1630a, was also included to allow calculation of method recoveries. The certified value for this CRM is shown in Table 2-1.

Table 2-1
Sample Composition

Sample Designation	Type	Classification	Source	Sulfur wt % dry basis	Ash wt % dry basis	Chlorine µg/g dry basis	HHV Btu/lb dry basis
Bailey	EPRI Coal	High Volatile A Bituminous	Pennsylvania	2.14	7.99	1059	13705
Meigs	EPRI Coal	High Volatile A Bituminous	Ohio	4.46	11.01	447	13020
Black Thunder	EPRI Coal	Subbituminous	Wyoming	0.46	7.81	134	11652
Jewett	EPRI Coal	Lignite	Texas	1.04	11.38	233	11190
Twenty Mile	EPRI Coal	High Volatile B Bituminous	Colorado	0.57	10.34	81	12361
Kayenta	EPRI Coal	High Volatile C Bituminous	Arizona	0.51	9.18	127	12197
NIST1630a	CRM Coal	High Volatile A Bituminous	USA	1.46	*7.16*	1144	13802

CRM - certified reference material
HHV - higher heating value
Shading indicates certified values; reference values are shown in italics

2.2 Laboratories

The five laboratories that took part in the study are listed in Table 2-2. Two of the laboratories are associated with the instrument vendor; the rest are commercial laboratories. One laboratory (COSA) analyzed the sample on two instruments. Each participant was assigned a lab code, which is used to identify data sets in this report. The samples were submitted to each of the study participants blind.

Table 2-2
Participating Laboratories

Laboratory	City	State	Country
Hawk Mountain Labs	West Hazleton	PA	USA
COSA Instruments A	Norwood	NJ	USA
COSA Instruments B	Norwood	NJ	USA
DIA Instruments	Kanagawa		Japan
Abimed	Langenfield		Germany
COSA Instruments	Houston	TX	USA

2.3 Data Acceptance

All results reported by laboratories were included in the data analysis, so long as the laboratory followed the study protocol. Laboratories were requested to repeat the analyses if they failed to follow the calibration or quality control requirements specified in the study protocol, or failed to conduct analysis of blind quality control samples distributed with the study materials.

2.4 Method Performance Characteristics

The same performance characteristics employed to evaluate chlorine methods in Phase 2 of the EPRI round robin study were used to evaluate the oxidative hydrolysis microcoulometry method. Table 2-3 shows the performance characteristics and the benchmarks that were used for each performance attribute.

Table 2-3
Method Performance Characteristics

Performance Characteristic	Benchmark
Multiple and single laboratory precision	Horwitz Equation
Bias	Percent recovery of chlorine with respect to certified values
Lower quantitative limit	Comparison with target limits based on chlorine levels in U.S. coal

Precision describes the closeness of agreement among test results. Bias is a measure of the systematic error between the mean of a set of test results and an accepted reference value. The certified reference value established for Standard Reference Material (SRM) coal 1630a by the U.S. National Institute of Standards and Technology (NIST) was used in this study to evaluate bias. The lower quantitative limit is the lowest concentration of a chemical that a method can measure with acceptable precision.

3 RESULTS

3.1 Study Results

Table 3-1 lists the chlorine results by oxidative hydrolysis microcoulometry, as reported by the five laboratories for the EPRI coals and NIST SRM coal 1630a.

Table 3-1
Chlorine Results, in µg/g dry basis

Lab Code	Bailey	Meigs	Twenty Mile	Black Thunder	Jewett	Kayenta	NIST 1630a
DB	1105	490	31	93	206	93	1105
	1138	485	33	90	223	86	1150
	1154	459	23	84	202	99	1131
	1182	469	23	91	207	90	1148
DD	1134	453	25	96	206	90	1120
	1139	456	27	98	223	91	1079
	1105	456	24	99	202	89	1129
	1127	455	26	95	207	92	1104
DC	1132	454	25	96	208	87	1094
	1157	457	21	98	207	86	1062
	1102	455	30	94	215	91	1062
	1138	460	27	95	200	89	1074
DE	1163	479	24	97	207	89	1103
	1096	474	24	92	204	87	1127
	1157	474	24	97	211	88	1068
	1144	485	24	95	209	87	1144
DA	1116	465	26	96	213	93	1153
	1148	484	24	92	214	90	1114
	1187	478	25	96	212	89	1138
	1184	493	26	93	210	93	1148
DF	1115	476	23	90	222	92	1096
	1068	461	23	91	224	83	1108
	1104	468	26	88	213	98	1087
	1103	448	25	83	210	98	1146

3.2 Multiple Laboratory Precision

Analytical precision can be expressed in terms of the standard deviation of multiple measurements of a sample. EPRI evaluated the analytical precision of the oxidative hydrolysis microcoulometry method against a widely accepted benchmark, the Horwitz equation, which is commonly used to evaluate the fitness for purpose of analytical methods.

The Horwitz equation expresses a regression relationship between the multiple laboratory relative standard deviation (RSD) and sample concentration. The equation was originally developed from over 6,000 method studies on a wide range of trace elements and matrices. If a method produces data with more than twice the RSD predicted by the Horwitz curve, this is a strong indication that the method is being applied below its lower limit of applicability.

The Horwitz equation takes the following form:

$$s_{Limit} = 0.02X_c^{0.8495}$$

where,

X_c is the weight fraction of the analyte in the sample

$X_c = 1$ for a pure analyte
$X_c = 0.000001$ for an analyte at 1 part per million

Multiplying s_{Limit} by the appropriate unit conversion factor yields the limiting standard deviation in the desired units. Multiplying by 1,000,000 would yield s_{Limit} in parts per million. For example, a sample with an analyte concentration of 100 parts per million (100 µg/g) would have a s_{Limit} of 8 µg/g. Twice this limit produces a Horwitz limit for this sample of 16 µg/g.

It should be noted that the Horwitz comparison indicates only whether a method exhibits adequate precision at the analyte concentrations present in the test samples. To determine the applicability of the method at the low end of the method range, a more rigorous benchmark must be applied: the lower quantitative limit.

Figure 3-1 compares the multiple laboratory precision of the oxidative hydrolysis microcoulometry method with the ASTM methods evaluated in Phase 2 of the EPRI mercury and chlorine round robin study. The Horwitz limits are shown by the black bars above each sample. A well-performing method should have a multiple laboratory RSD below the Horwitz limit.

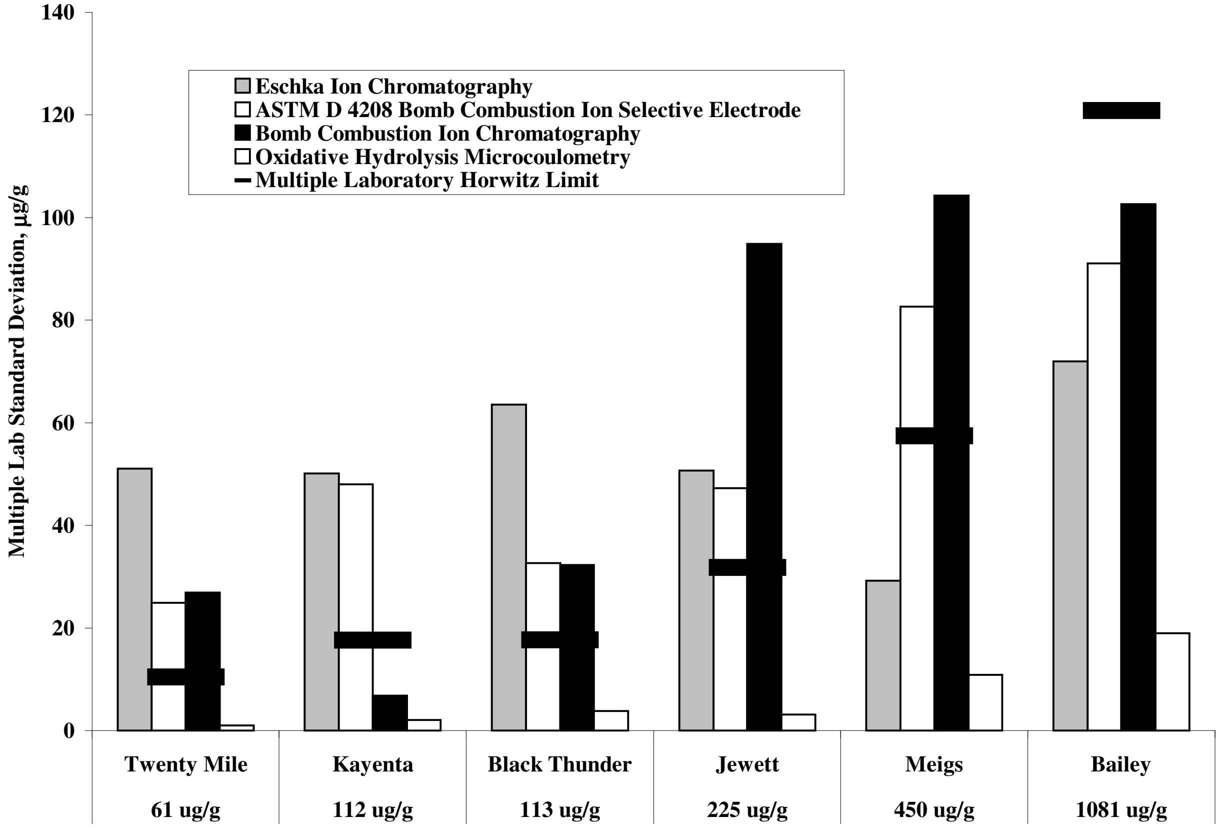

Figure 3-1
Multiple Laboratory Precision Chlorine Methods

It is evident from Figure 3-1 that the multiple laboratory precision of the oxidative hydrolysis microcoulometry method is a significant improvement over that of current ASTM methods.

3.3 Single Laboratory Precision

The Horwitz equation can also be used to evaluate precision within a laboratory, based on the empirical observation that the single-laboratory limiting standard deviation is typically about half of the multiple-laboratory limiting standard deviation.

Figure 3-2 compares the single laboratory precision of the oxidative hydrolysis microcoulometry method with the ASTM methods evaluated in Phase 2 of the EPRI mercury and chlorine round robin study. The Horwitz limits are shown by the black bars above each sample.

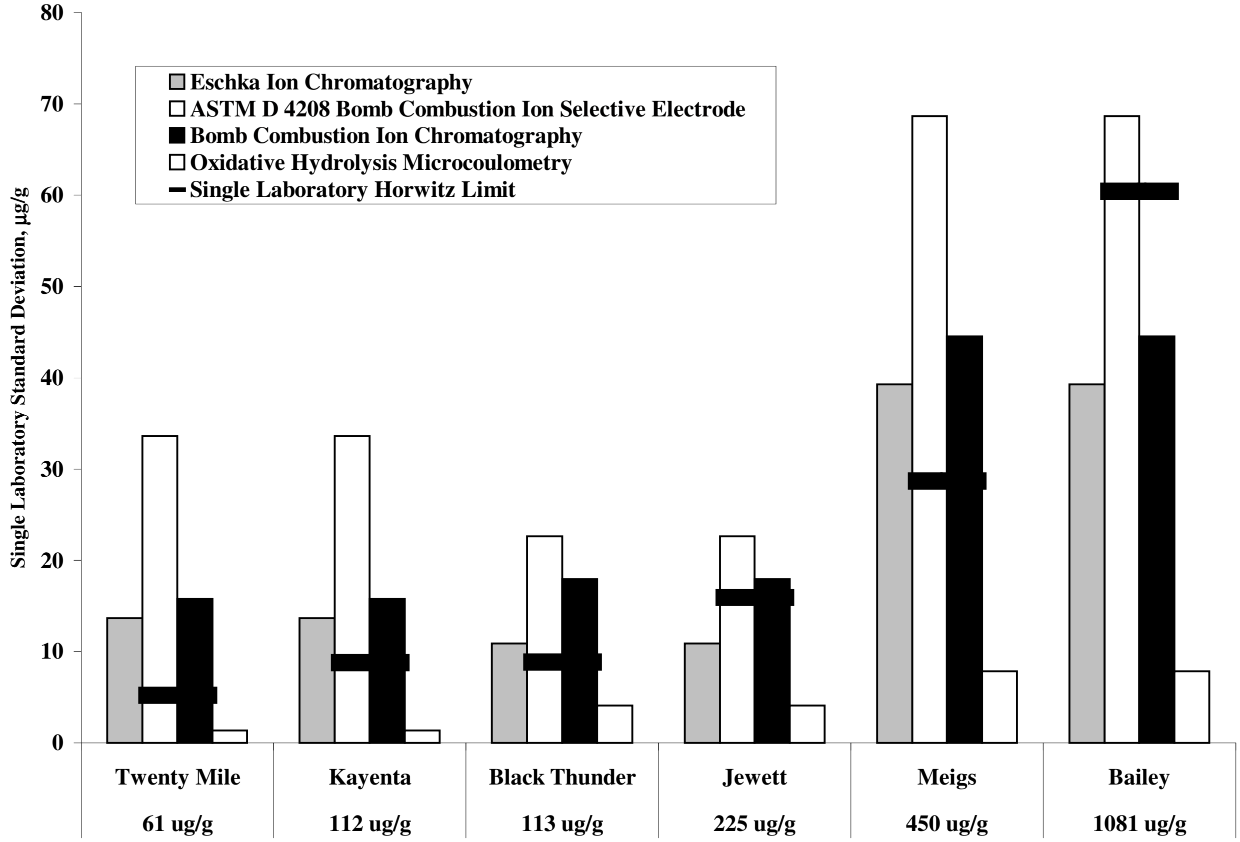

Figure 3-2
Single Laboratory Precision Chlorine Methods

Again, it is evident from Figure 3-2 that the single laboratory precision of the oxidative hydrolysis microcoulometry method is much better than that of current ASTM methods.

3.4 Bias of Chlorine Methods

One of the study samples, NIST SRM 1630a, has a certified chlorine value of 1144 µg/g with an uncertainty of ± 32 µg/g. Figure 3-3 compares the average and 95% uncertainty limits for the oxidative hydrolysis microcoulometry method and the ASTM methods with the SRM 1630a value and uncertainty limits. Of the three ASTM methods, only ASTM D 4208 Bomb Combustion Ion Selective Electrode produces a chlorine average within the uncertainty limits specified by NIST. Only the Eschka Ignition method yields limits of uncertainty narrower than those established by NIST; however, the Eschka procedure is clearly biased low. Oxidative hydrolysis microcoulometry not only yields an average result within the uncertainty limits specified by NIST but also with narrower uncertainty limits than established by NIST. However, the oxidative hydrolysis microcoulometry procedure does appear to be biased slightly low.

The certificate issued by NIST for SRM 1630a states that the certified value for chlorine was determined in part by INAA and the dry basis value was calculated from moisture values determined in nitrogen. The moisture values used to determine the dry basis values for the oxidative hydrolysis microcoulometry procedure were determined in air. Drying in air produces lower moisture values than drying in nitrogen and this could account for the bias.

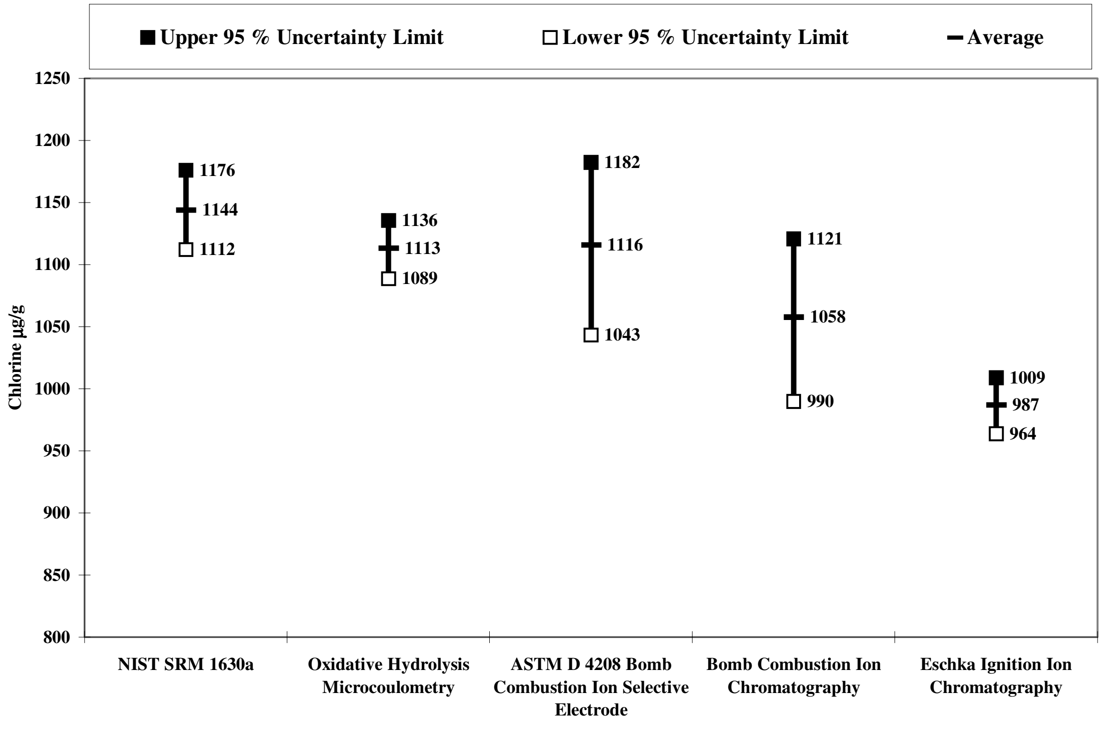

Figure 3-3
Bias of Chlorine Methods

3.5 Lower Quantitative Limit of Chlorine Methods

ASTM E 1601, *Standard Guide for Interpretation and Use of Results from Interlaboratory Testing of Chemical Analysis Methods*, defines the lower quantitative limit (L) as the concentration in a material below which a method may not be used to report quantitative values. L is calculated according to the equation:

$$L = 100R/e_{max} \qquad (1)$$

where;

R is the Reproducibility Index calculated according to ASTM E 1763[4]
e_{max} is the maximum acceptable relative percent error

ASTM E 1601 states that an e_{max} value of 50% yields values for L useful for determining residual levels of trace elements.

The target chlorine concentration for L was set at 100 µg/g for this study, based on the lowest levels of chlorine typically observed in U.S. thermal coals.

Figure 3-4 compares the lower quantitative limit of oxidative hydrolysis microcoulometry with the ASTM methods, calculated according to ASTM E 1763. It is obvious from Figure 3-4 that the oxidative hydrolysis microcoulometry produces a lower quantitative limit well below the specified target limit and an order of magnitude better than any of the ASTM methods.

Table 3-2 compares the performance measures for chlorine over the entire range of samples examined. It clearly reveals that the oxidative hydrolysis microcoulometry procedure is a significant improvement over current ASTM methods. For example, below 50 µg/g chlorine the between and within laboratory RSD for the ASTM methods are 15 to 25 times higher than for the oxidative hydrolysis microcoulometry procedure.

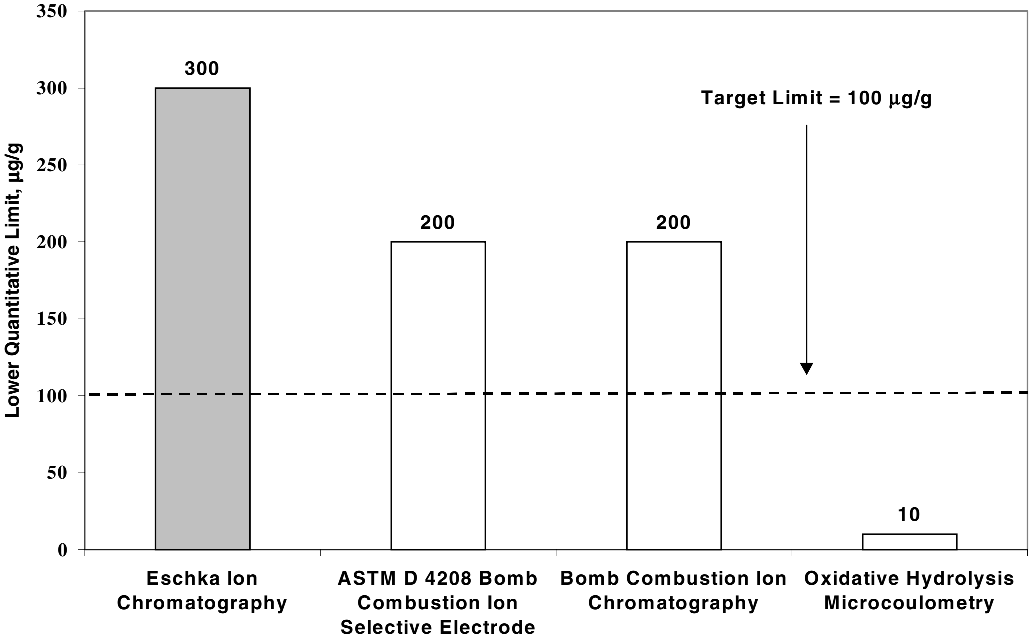

Figure 3-4
Lower Quantitative Limits of Chlorine Methods

Table 3-2
Performance Summary for Chlorine Methods

Chlorine µg/g	Oxidative Hydrolysis Microcoulometry		ASTM D 4208 Bomb Combustion Ion Selective Electrode		Bomb Combustion Ion Chromatography		Eschka Ignition Ion Chromatography	
	L =10 µg/g		L =200 µg/g		L =200 µg/g		L =300 µg/g	
	NIST 1630a Recovery = 97 %		NIST 1630a Recovery = 98 %		NIST 1630a Recovery = 92 %		NIST 1630a Recovery = 86 %	
	$RSD_{Between}$	RSD_{Within}	$RSD_{Between}$	RSD_{Within}	$RSD_{Between}$	RSD_{Within}	$RSD_{Between}$	RSD_{Within}
5	40%	40%	800%	600%	580%	400%	1060%	200%
10	20%	20%	400%	300%	290%	200%	530%	100%
50	4%	4%	80%	60%	60%	40%	106%	20%
100	3%	2%	40%	30%	32%	20%	53%	10%
200	2%	2%	20%	15%	20%	10%	27%	10%
300	2%	1%	17%	13%	17%	7%	18%	7%
400	2%	1%	13%	13%	16%	8%	14%	5%
500	2%	1%	12%	10%	15%	6%	11%	6%
600	2%	1%	12%	10%	15%	5%	9%	5%
800	2%	1%	11%	10%	15%	5%	7%	5%
1000	2%	1%	10%	9%	14%	5%	6%	5%

L = Lower quantitative limit

$RSD_{Between}$ = Relative standard deviation of multiple laboratory data

RSD_{Within} = Relative standard deviation of single laboratory data

4 CONCLUSIONS

This study compared the most commonly used methods for the determination of chlorine in coal with a new method based on oxidative hydrolysis microcoulometry.

None of the ASTM chlorine methods achieve the target lower quantitative limit of 100 µg/g. The limits for the methods ranged from 200 to 300 µg/g. In addition, the ASTM methods generally did not meet performance criteria for measurement variability between laboratories and yield inconsistent results with respect to chlorine recoveries.

The oxidative hydrolysis microcoulometry procedure, which was evaluated against the same series of coals as the ASTM methods, not only meets but also significantly surpasses the performance criteria.

The oxidative hydrolysis procedure requires no chemical treatment of the sample, and a single result can be generated in about ten minutes using as little as 10 mg of 60 mesh (250 µm) coal. The instrument can be used with an autosampler for multiple analyses. The modified instrument used in this method is currently available from only one U.S. distributor, COSA Instruments of Norwood, New Jersey. Based on the findings of this study, it is concluded that this method offers a very significant increase in performance over current ASTM methods for analysis of chlorine in coal. The quality of the results are comparable to those obtained with INAA and the method is more readily adaptable to routine laboratory use.

Limitations of this study were the relatively small number of participating laboratories. In addition, the method was not tested on a high-ash (>16% ash) coal; analytical difficulties were observed with high-ash coals using all of the ASTM methods. EPRI suggests that power producers using the oxidative hydrolysis microcoulometry method request the laboratory to analyze several SRMs of different coal type along with the submitted samples, to better characterize the method performance.

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