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METHOD FOR DETERMINING SULFUR AS SULFUR DIOXIDE

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ABSTRACT OF THE DISCLOSURE

Chloride compound and nitrogen interferences to the iodometric and/or microcoulometric methods of sulfur determination are overcome by adding sodium azide to the titration cell electrolyte. The improved method is applicable to oils, crudes, solids, and petrochemicals.

BACKGROUND OF THE INVENTION

The presence of chlorine in concentrations in excess of 1.0% and nitrogen in excess of 0.1% may interfere in the iodometric determination of sulfur in petroleum and chemical products using the classical iodometric ASTM Method of Test for Sulfur in Petroleum Products (High Temperature Method) (D 1552–64) or its equivalent. In the case of nitrogen, the extent of such interference is dependent on the type of nitrogen compound as well as the amount present. The interference results from oxidation of nitrogen to oxides of nitrogen and chloride to chlorine, each of which reacts with potassium iodide in the iodometric titration to liberate iodine. Sulfur is oxidized in the method to sulfur dioxide which is measured by the consumption of iodine in the titration. Therefore, the effect of the presence of nitrogen and chlorine is to cause low, or even negative results. Since chloride and especially nitrogen are commonly associated with sulfur in petroleum products, petrochemicals, and chemicals, this interference constitutes a very severe limitation of the method.

Therefore, it is one object of this invention to provide an improved method for determining sulfur as sulfur dioxide in petroleum and chemical products. It is another object of this invention to provide a method of overcoming nitrogen and chloride compound interferences in the classical methods of sulfur determination so that the inherent limitations of the old methods are eliminated.

In one embodiment, our invention provides an improvement in the method for determining sulfur as sulfur dioxide in petroleum, petrochemical, and chemical products utilizing the iodometric or microcoulometric methods of sulfur determination wherein a titration cell containing an iodine-containing titration solvent is utilized, said improvement comprising overcoming chloride compound and nitrogen interferences in said method by adding sodium azide to the titration solvent thereby preferentially reacting the chloride compounds and nitrogen compounds without reacting the iodine.

SUMMARY OF THE INVENTION AND EXAMPLE

In order to overcome the interference from nitrogen, several scrubbers and pretreatments were evaluated. From this experimentation, it was found that an alkali metal azide, and preferably sodium azide, added directly to a titration vessel, appeared to react rapidly and preferentially with chlorine and the oxides of nitrogen. The presence of sodium azide did not appear to otherwise participate in or interfere with the iodometric determination of sulfur as sulfur dioxide. To check these preliminary observations, several standards were analyzed with and without the presence of sodium azide in the titration vessel of the volumetric-type sulfur determinator, and in the coulometric-type sulfur analyzer as described in Adams et al., "Improved Sulfur-Reacting Microcoulometric Cell for Gas Chromatography," Analytical Chemistry, vol. 38, 1966, p. 1094.

An induction furnace and automatic volumetric sulfur apparatus was used where the test method called for a volumetric-type sulfur determinator. A microcoulometer with a 300 P cell was used for iodine generation where the method called for a coulometric-type sulfur analyzer. The combustion train used with the microcoulometer employed a 13 mm. outside diameter, 10 mm. inside diameter, 115-cm. quartz tube filled with quartz chips, coarsely ground to pass a ⅛ inch screen. The quartz tube was maintained at 1150° C. using two heavy duty combustion furnaces in series. Oxygen carrier flow rates from 20 to 300 ml./min. were preferred, although a flow of 50 ml./min. was normally used with this apparatus. Sodium azide (practical) was used as the reagent.

For the coulometric analyses, 3 to 5 mg. of solid sodium azide was added to the titration cell solvent. In order to equilibrate the system prior to the first determination, a sample of SO_2 gas was injected or a sample of the product was burned. A fresh portion of sodium azide was added whenever the cell solvent was changed.

For the volumetric-type determinations, 500 to 700 mg. of solid sodium azide was added to the titration cell solvent prior to each determination. No other changes in the normal operating procedures for the method are required for either approach to the iodometric sulfur analysis. To determine the efficacy of sodium azide addition in overcoming nitrogen and chlorine interference, several standards and samples were analyzed with and without added sodium azide. The data in Table 1 comparing both the coulometric and volumetric methods were obtained:

Therefore, it can be concluded that sodium azide added to an iodine-containing titration solvent is effective in overcoming the interference from chloride compounds and nitrogen where it is encountered in the iodometric determination of sulfur as sulfur dioxide. For ASTM Method D 1552 modified by the improvement of my invention, the relative error in the presence of about 20% chlorine and about 8% nitrogen was −2.2%; the relative standard deviation was 2% for the 1 to 20% sulfur level. For the coulometric sulfur method, the relative error in the presence of about 8% nitrogen was about −1.0% and the relative standard deviation was 1.1%. As shown below, samples analyzed included oils, crudes, and solids and included sulfur levels ranging from about 0.1 to about 20%. The coulometric method is more sensitive and has better precision than the volumetric method although the two methods are comparable in accuracy, even in the presence of large amounts of nitrogen and chlorine compounds provided the improvement of my invention, namely, the addition of sodium azide to the titration solvent is utilized.

TABLE 1.—ANALYSIS OF STANDARDS AND SAMPLES WITH AND WITHOUT ADDED SODIUM AZIDE

Sample	Percent present			Percent sulfur found			
				No NaN_3 added		NaN_3 added	
	Cl	N	S	Volumetric	Coulometric	Volumetric	Coulometric
Cysteine hydrochloride	20.24	7.98	18.25	[1] Black	Negative [1]	18002, 18.10	
Benzenesulfonamide	0	8.90	20.39	[1] Black	do [1]	20.29, 20.53	
$C_{12}SH$ in Nujol standard		0.0	0.0	0.0		0.0	
Do		0.0	2.15	2.09, 2.12		2.11, 2.12	
Do		0.5	2.13	2.03, 2.00		2.07, 2.08	
Do		2.6	2.13	1.83, 1.87		2.13, 2.12	2.16, 2.12
Do		5.3	1.05	0.65, 0.82		1.11, 1.07	1.06, 1.12
Asphaltene, Sample 1						5.08	4.92
Asphaltene, Sample 2						5.43	5.67
Asphaltene, Sample 3						4.38	4.48
t-$C_{12}SH$ in Nujol standard			0.1200			0.12	0.1200, 0.1207 0.1228, 0.1196 0.1202
Heavy oil, Sample 1						1.25	1.36, 1.34
Heavy oil, Sample 2						0.14, 0.15, 0.14, 0.17, 0.15, 0.13, 0.16, 0.15	0.1533, 0.1591 0.1521, 0.1547 0.1573
Solid catalyst, spent				2.44		3.31, 3.31	
Crude oil			2.16, [2] 2.19			2.16	2.18, 2.17

[1] Generates iodine; gives black solution in the volumetric method and a negative response in the case of the coulometric method if much nitrogen is present.

[2] Oxygen bomb analysis, ASTM Method of Test for Sulfur in Petroleum Products by the Bomb Method (D 129-64).

I claim:

1. In a method for determining sulfur as sulfur dioxide in petroleum, petrochemical, or chemical products which contain sulfur, nitrogen and chlorine utilizing the iodometric or microcoulometric methods of sulfur determination wherein a titration cell containing an iodine-containing titration solvent is utilized to measure sulfur dioxide by consumption of the iodine, the improvement which comprises adding an alkali metal azide to said titration solvent thereby preferentially reacting said chlorine and nitrogen without reaction of said iodine.

2. The method of claim **1** wherein said alkali metal azide is sodium azide.

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