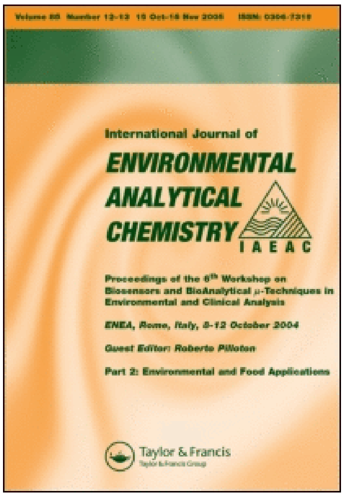

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ANALYSIS OF TOTAL NON-VOLATILE NON-SULFIDE REDUCED SULFUR IN POTABLE AND UNTREATED SURFACE AND GROUNDWATERS

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An analytical method was developed to measure the total concentration of non-volatile non-sulfide reduced sulfur in treated and untreated surface and groundwater. The method was based on the alkaline reduction by Raney nickel (prepared *in situ* from Raney alloy) of organic and inorganic sulfur compounds (in oxidation states below +6) to sulfide. Sulfide was swept out of the reflux apparatus under nitrogen into a trap of zinc acetate and determined colorimetrically as ethylene blue. The recoveries obtained from solutions of elemental sulfur, sulfide, sulfite, thiosulfate, tetrathionate, cysteine, cystine, methionine, glutathione, allylthiourea, sulfanilamide and thiocyanate ranged from 84–102% with typical recoveries of approximately 90%. Sulfate was not detectable by the procedure. Chlorine present in potable water samples interfered in the procedure and was removed with sodium borohydride. The relative standard deviation of the method varied from 0.25 to 5.6% and averaged 3%. The detection limit based on a 500 mL sample was 3 mg m^{-3}.

Keywords: Analysis; potable water; groundwater; reduced sulfur compounds; reduction; swampy odour

INTRODUCTION

The water supply to Perth, Western Australia, is drawn from protected surface water catchments and from shallow and artesian groundwater. Since 1980, some consumers supplied with water from two of the four groundwater treatment plants have complained of an intermittent swampy or cooked vegetable odour.[1] This odour, which is caused by dimethyl trisulfide which has an odour threshold of about 10 $\mu g\ m^{-3}$, is not present in treated surface water or untreated groundwater, nor within the treatment plant, but develops in the water distribution

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*Corresponding author. Fax: +61-8-9362-5627 system. The problem is invariably associated with low chlorine concentrations and typically occurs at the extremities of the distribution system.

The mechanism of dimethyl trisulfide generation in the water distribution system is not yet known. However, sulfur compounds are likely to be precursors. The dominant sulfur species in both treated and untreated surface and groundwater waters in Perth is sulfate with concentrations in the range 5–80 g m^{-3}. It is thus unlikely that sulfate is the critical species with respect to swampy odour generation. As treated waters are chlorinated prior to entry to the distribution system, concentrations of sulfide are also negligible. Attention was thus focussed on sulfur compounds other than sulfide or sulfate which might be present in differing amounts in the various water supply schemes, and which may therefore affect the generation of dimethyl trisulfide.

A range of reduced sulfur compounds is likely to be present in surface and groundwaters. At the present time, methods are available to specifically determine only a few individual inorganic and organic non-volatile reduced sulfur compounds, such as sulfide. A method was therefore sought which could give a gross measure of the total non-volatile reduced sulfur content of potable waters. Methods are available to determine total sulfur in water, but these also include sulfate. A method was thus needed which could measure the total amount of non-volatile sulfur compounds other than sulfate and sulfide, referred to generically in this paper as non-volatile non-sulfide reduced sulfur compounds.

Granatelli[2] used a Raney nickel reduction procedure for the determination of reduced sulfur in non-alkene hydrocarbon materials. Lowe and Delong[3] used a procedure to determine carbon-bonded sulfur in Canadian soils in which Raney nickel was generated *in situ*. Freney *et al.*[4] used these procedures as well as their own to measure carbon-bonded sulfur in Australian soils. They reported 97–100% recovery of elemental sulfur, sulfur oxyanions (other than sulfate and dithionate) and a range of organic sulfur compounds including sulfur amino acids, sulfoxides and aromatic sulfonic acids.

Kijowski and Steudler[5] developed an analytical procedure for the determination of non-volatile non-sulfide reduced sulfur in salt marsh waters based on the alkaline reduction by Raney nickel of organic and inorganic sulfur compounds (in oxidation states below +6) to sulfide. However, this method was based on a sample volume of 50 mL and had a detection limit of 25 mg m^{-3}. This detection limit was too high for our purposes where non-sulfide reduced sulfur concentrations in water at the consumer's tap were less than 20 mg m^{-3}. Further, the Raney nickel powder used by Kijowski and Steudler was not available in Australia.

A more general procedure, adapted from that developed by Kijowski and Steudler[5], was thus developed for the determination of the total concentration of non-volatile non-sulfide reduced sulfur which was suitable for use with both potable and untreated surface and groundwaters. This paper reports the development of that procedure.

METHODOLOGY

Water samples (500 mL) were collected in all-glass bottles to which 22% zinc acetate dihydrate (AR, Ajax Chemicals, Australia) solution (1 mL) was added at the time of collection. If the sample contained chlorine, sodium borohydride (20 mg) (BDH Chemicals, England) was also added. The sample was transferred to a 1 L 3-necked round-bottom flask and 24% sodium hydroxide (AR, Sigma Chemicals, USA) solution (5 mL) was added. After the sample was purged with oxygen-free, high-purity nitrogen (CIG, Australia), Raney alloy (50:50 nickel: aluminium, 0.500 g precisely weighed) (Fluka, Switzerland) was added. The sample was then refluxed for 40 minutes under nitrogen. Raney nickel was formed during the reflux and organic and inorganic sulfur compounds in oxidation states lower than +6 were reduced to sulfide.

After cooling, the reaction mixture was acidified dropwise with concentrated hydrochloric acid (50 mL). The hydrochloric acid (500 mL) (AR, Ajax Chemicals, Australia) had previously been treated with tightly folded aluminium foil (1 g) (BDH Chemicals, England), and filtered. The sample was refluxed for 1 hour, and the hydrogen sulfide formed was swept into a water trap (80 mL) containing 22% zinc acetate dihydrate solution (2 mL). After sequential addition of N,N-diethyl-p-phenylenediamine sulfate (BDH Chemicals, England) and ferric ammonium sulfate dodecahydrate (Unilab, Ajax Chemicals, Australia) to the trap, stirred gently but thoroughly between additions, the sulfide in the trap was determined colorimetrically as ethylene blue.[6]

Any sulfide originally present in the sample was determined separately from non-sulfide reduced sulfur by preliminary acidification and stripping into a water trap (80 mL) containing 22% zinc acetate dihydrate solution (2 mL), prior to the alkaline reflux.

The technique is shown diagramatically in Figure 1.

Recoveries of sulfur from sodium sulfide nonahydrate (AR, Ajax Chemicals, Australia), sodium thiosulfate (99.5%, Aldrich, Australia), sodium tetrathionate dihydrate (98%, Aldrich, Australia), L-cysteine hydrochloride (Ajax Chemicals, Australia), cystine (98.5%, BDH Chemicals, England), L-methionine (BDH Chemicals, England), glutathione (98%, Aldrich, Australia), allylthiourea (98%,

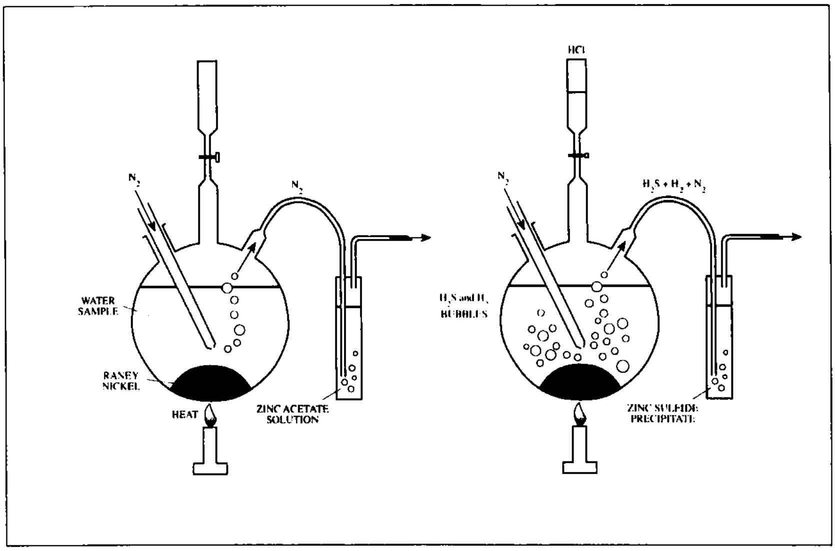

FIGURE 1 Apparatus for non-sulfide reduced sulfur determination

Aldrich, Australia), sulfanilamide (98%, Aldrich, Australia), sodium thiocyanate (98%, Aldrich, Australia) and sodium sulfate (AR, Ajax Chemicals, Australia) were determined by adding an aqueous solution of the pure compound to water (500 mL). Recovery of elemental sulfur (AR, Ajax Chemicals, Australia) was determined by adding the pure compound dissolved in xylene to water (500 mL). Recovery of sodium sulfite was determined by adding the pure compound to boiled, nitrogen-purged water (500 mL).

The colorimetric determination of sulfide was standardised against solutions of freshly prepared sodium sulfide nonahydrate (AR, Ajax Chemicals, Australia) in boiled, nitrogen-purged deionised water. The sulfide was standardised against a solution of iodine acidified with two drops of concentrated hydrochloric acid[7] using starch indicator powder (BDH Chemicals, England). The iodine solution was prepared from re-sublimed iodine (Unilab, Ajax Chemicals, Australia) and potassium iodide (AR, BDH Chemicals, England) and standardised against sodium thiosulfate (Univol, Ajax Chemicals, Australia) acidified with two drops of concentrated hydrochloric acid.[7] The sodium thiosulfate solution was standardised against potassium iodate (AR, BDH Chemicals, England) to which potassium iodide (1g) and 2N sulfuric acid (AR, BDH Chemicals, England) (2 mL) were added.

RESULTS AND DISCUSSION

Recovery of Sulfur from Standard Sulfur Compounds

The recoveries of sulfur obtained from solutions of elemental sulfur, sulfide, sulfite, thiosulfate, tetrathionate, cysteine, cystine, methionine, glutathione, allylthiourea, sulfanilamide and thiocyanate at concentrations ranging from 20–72 mg sulfur m^{-3} are shown in Table I.

Average recoveries from this large variety of different types of sulfur compounds ranged from 84–102% with typical recoveries of approximately 90%. Recovery of 3–15 g sulfate-sulfur m^{-3} in the procedure was zero, demonstrating that the method did not measure sulfate.

These recoveries are similar to but slightly lower than those reported in previous studies.[4,5] Less than quantitative recoveries could not be attributed to incomplete reduction of sulfur compounds by the Raney nickel as recovery of sulfide itself was similar to that of other reduced sulfur compounds. Less than complete recoveries were also not due to trap inefficiencies as no sulfide was found in a second zinc acetate trap placed in series. It is also unlikely to be due to oxidation of sulfide formed *in situ* as no difference was found when ultrapure nitrogen was used to purge the apparatus, or when the nitrogen was passed through an oxygen trap.

To determine the recovery of elemental sulfur, it was dissolved in chloroform and then added to water because of the difficulty of achieving complete dissolution of sulfur in water directly. However, recoveries of elemental sulfur dissolved in chloroform were poor (60–77%), possibly because the sulfur separated from solution as the chloroform boiled off during the reflux. Recoveries of elemental sulfur dissolved in xylene were much better (82–97%) and were similar to those obtained for other sulfur compounds, possibly because xylene has a higher boiling point than chloroform and did not boil off during the reflux. In natural waters, elemental sulfur would probably be present either in a colloidal form or in solution as polysulfide, so this problem would not exist, and recoveries would be expected to normal. Tests in which xylene was added to natural waters presumed to contain elemental sulfur showed that xylene had no effect on the concentration of non-volatile non-sulfide reduced sulfur determined.

Initially, with new apparatus, recoveries were poor, probably due to adsorption of sulfide on the glass surfaces. However, once the apparatus had been used to analyse solutions containing more than 25 mg sulfide sulfur, recoveries were consistently high.

TABLE I Recovery of standard sulfur compounds (%)

Sulfur compound	*Deionised water*			*Dechlorinated deionized water**			*Untreated groundwater†*			*Clarified groundwater***			*Tap water††*		
	Range	*Average*	*n*	*Range*	*Average*	*n*	*Range*	*Average*	*n*	*Range*	*Average*	*n*	*Range*	*Average*	*n*
Sulfide	85–101	93	9												
Elemental sulfur	82–97	91	11	86–90	87	4	80–97	88	10	96	96	1	91	91	1
Thiosulfate	84–103	93	8	79–101	92	6	78–105	92	14	77–104	90	9	83–102	94	8
Sulfite	79–90	84	4												
Tetrathionate	99–100	100	2												
Cysteine	86–97	91	8	82–91	88	4									
Cystine	96–99	98	2												
Methionine	88–93	91	5												
Glutathione	92–107	99	3	89	89	1	101	101	1	80–113	96	2	102	102	1
Allythiourea	98–102	100	2												
Sulfanilamide	99–101	100	2												
Thiocyanate	89–96	92	2												
Sulfate	0	0	2												

* Chlorinated water dechlorinated with sodium borohydride
† Unchlorinated or chlorinated groundwater
** Clarified chlorinated or unchlorinated groundwater
†† From distribution system

TABLE II Effect of dechlorination on recovery of reduced sulfur

Sample	*Free chlorine* $g\ m^{-3}$	*Total chlorine* $g\ m^{-3}$	*Dechlorinating agent used*	*Non-volatile non-sulfide reduced sulfur* $mg\ m^{-3}$
Treated	1.20	1.50	none	9
water	0	0	0.07 mg sodium arsenite	15
Treated	0.40	0.50	none	24
water	0	0	0.58 mg iron (II)	39

Effect of Raney Nickel

Kijowski and Steudler[15] used commercially available prepared Raney nickel powder (PCR No. 10038, Gainesville, Florida). This was no longer available when we began to use their method, so we initially attempted to prepare our own Raney nickel from Raney alloy.[18] However, the Raney nickel prepared in our laboratory suffered considerably from variations in activity and in the magnitude of the procedural blanks between batches.

It was therefore ultimately decided to form the Raney nickel *in situ* during the alkaline reduction procedure. This eliminated the need for tedious catalyst preparation procedures, eliminated variations in activity of the catalyst with time or batch, and allowed precisely weighed dry metal to be added, allowing the procedural blank to be more accurately determined. This procedure also would be expected to produce the strongest desulfurising catalyst.[19]

Typically, the non-volatile non-sulfide reduced sulfur content of the Raney nickel used was 7.3 μg sulfur per gram of alloy, resulting in a procedural blank of 7.3 mg sulfur m^{-3}.

Effect of Chlorine

Chlorine present in water samples interfered in the procedure, as shown by the concentration of non-volatile non-sulfide reduced sulfur measured in chlorinated waters with and without the addition of a reducing agent (Table II).

Dechlorination of chlorinated samples using sodium arsenite, ascorbic acid and ferrous iron all resulted in higher recoveries of non-sulfide reduced sulfur. However, addition of any of these reagents resulted in lower recoveries than in the standard procedure. For example, recovery of thiosulfate from deionised water after adding arsenite was only 65%, while recovery of methionine in the presence of iron (II) was only 63–80% and recovery of thiosulfate in the presence of ascorbic acid was only 70–80%. Arsenates are mild oxidising agents in acid solution, while iron (III) can oxidise hydrogen sulfide.[14] It is thus possible

TABLE III Recovery of reduced sulfur in solutions dechlorinated with sodium borohydride

Sulfur compound	*Recovery from standard procedure (%)*	*Recovery from solution dechlorinated with sodium borohydride (%)*	*Recovery from solution containing only sodium borohydride (%)*
Thiosulfate	84–103 (n = 6)	79–96 (n = 4)	93–101 (n = 2)
Cysteine	86–91 (n = 2)		82–88 (n = 2)
Glutathione	92	89	

that these dechlorinating reagents interfere with the method through oxidation of the hydrogen sulfide liberated during the acid stripping stage of the procedure.

Recoveries of reduced sulfur compounds in solutions dechlorinated with 0.3–24 mg sodium borohydride prior to addition of the sulfur compound or only containing sodium borohydride are presented in Table III.

These results indicated that recoveries in solutions dechlorinated with sodium borohydride or containing sodium borohydride were comparable to those achieved in samples which did not contain sodium borohydride or had not contained any chlorine. Consequently, approximately 20 mg of sodium borohydride was added at the time of collection to all water samples containing chlorine.

Effect of Storage

Table IV presents data showing the effect of storage time on the measured concentrations of non-sulfide reduced sulfur in untreated and treated groundwater samples. Zinc acetate and sodium borohydride were added at the time of sample collection, and the samples were stored at 4°C until analysed.

TABLE IV Effect of storage time on concentration of non-volatile non-sulfide reduced sulfur

Sample	*Storage time (day)*	*Non-volatile non-sulfide reduced sulfur initially (mg m^{-3})*	*Non-volatile non-sulfide reduced sulfur after storage (mg m^{-3})*
Untreated groundwater	1	414	352
Groundwater after aeration	0.5	268	261
Groundwater before clarification	1	240	236
Groundwater after clarification	1	56	56
Groundwater after filtration	1	55	60
Groundwater after chlorination	1	41	37

TABLE V Results of duplicate analyses of non-volatile non-sulfide reduced sulfur in groundwater

Sample	*Non-volatile non-sulfide reduced sulfur (mg m^{-3})*	*Average non-volatile non-sulfide reduced sulfur (mg m^{-3})*	*Relative standard deviation (%)*
Untreated groundwater	272,273	272.5	0.25
Untreated groundwater	166,173	167.5	2.9
Untreated groundwater	256,252	254	1.1
Chlorinated groundwater	426,416	421	1.7
Chlorinated groundwater	366,396	381	5.6
Groundwater after chlorination	57,60	58.5	3.6
Groundwater after chlorination	89,96	92.5	5.4

These results indicated that non-volatile non-sulfide reduced sulfur concentrations were stable for at least 24 hours if samples were dechlorinated and stored under refrigeration.

Precision and Detection Limit

The precision of the method was determined by duplicate analysis of a range of untreated and treated groundwaters. These results are presented in Table V. These results indicated that the relative standard deviation varied from 0.25 to 5.6% and averaged 3%.

The linear range of the procedure was at least 0–40 μg sulfur; water samples could be diluted if required to bring them within this range. The detection limit for sulfide was 1 mg m^{-3}, based on a 500 mL sample and an absorbance against a reagent blank of 0.01 using a 10 mm path length cell for determination of the ethylene blue colour. The detection limit (95% confidence interval) for non-volatile non-sulfide reduced sulfur was 3 mg m^{-3}, based on a 500 mL sample and on an absorbance 4.65 times the standard deviation of the Raney nickel blank.[10]

CONCLUSIONS

An analytical procedure was developed which was capable of determining sulfide sulfur and non-volatile non-sulfide reduced sulfur in treated and untreated ground and surface waters. It did not measure sulfate. The limit of detection of non-volatile non-sulfide reduced sulfur was 3 mg m^{-3}.

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