Analytical Methods for the Detection of Osmium Tetroxide: A Review

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Abstract

A strong oxidizer, osmium tetroxide (OsO_4) is a highly toxic and irritative species. Its volatility enhances the risk of intoxication by inhalation in areas with poor ventilation. Osmium tetroxide attacks mainly skin, mucous membranes, nose, and eyes at very low concentrations. These are the main reasons why osmium tetroxide may be abused as a chemical weapon in public areas with limited air circulation (airports, shopping centres). Therefore, stringent monitoring is needed. Analytical methodologies, approaches, and strategies for the detection of osmium tetroxide are comprehensively surveyed in the proposed work.
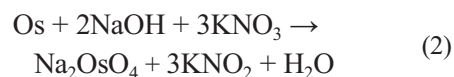
Introduction

Osmium tetroxide is one of the few chemical compounds containing an atom with oxidation number VIII. Moreover, it includes osmium, an element that is naturally very rare, occurring dispersed in the presence of other noble metals. Therefore, it would seem that osmium compounds rank among the exotic substances, without any practical significance. Proof that this is a misleading opinion may serve this paper where physicochemical and toxicological properties, together with health effects of osmium tetroxide, are discussed. Its volatility and toxicity could be abused for criminal purposes, which may cause serious problems for public safety.

Osmium tetroxide is one of the three known oxides in which metal exists in the highest oxidation state (together with ruthenium and xenon). Metallic osmium is usually covered with a thin layer of osmium tetroxide as a product of its oxidation with an aerial oxygen:

$$Os + 2O_2 \rightarrow OsO_4 \qquad (1)$$

Reaction (1) is very slow. The best conditions for the oxidation of the powdered osmium metal are at 800ºC, where osmium is oxidatively melted with a mixture of NaOH and alkaline nitrate (2). Osmate (VI) formed in this reaction is disproportionate in the acidic conditions to oxides (3).

$$Os + 2NaOH + 3KNO_3 \rightarrow \\ Na_2OsO_4 + 3KNO_2 + H_2O \qquad (2)$$

$$2OsO_4^{2-} + 4H_3O^+ \rightarrow OsO_4 + OsO_2 + 6H_2O \qquad (3)$$

Some physicochemical properties are listed in Table 1. Osmium tetroxide vapours have a characteristic unpleasant chlorine odour [1]. Saturation vapour pressure of OsO_4 at 20ºC is 0.93 kPa (7 mm Hg) and 5.2 kPa at 50ºC. These values show that it sublimes easily at room temperature and evaporation increases with increasing temperature.

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Table 1. Some physicochemical properties of OsO_4.

Physicochemical properties	Appearance	Molecular weight ($g \cdot mol^{-1}$)	Melting point (ºC)	Boiling point (ºC)	Liquid Density ($g \cdot cm^{-3}$)	Solubility at 25ºC ($g \cdot l^{-1}$)
OsO_4	colorless to yellowish solid	254.23	40.25	130	4.9	60

Table 2. Comparison OsO_4 vapor pressures with water and typical chemical warfare agents.

T [ºC]	Saturation vapour pressure (kPa)							
	water	OsO_4	sarin	soman	VX	phosgene	cyclosarin	HCN
0ºC			0.07	0.06			0.8	34.2
20ºC	2.27	0.93	0.28	0.05	0.06	0.9	5.9	82.6
25ºC		1.31			0.09	1.3	9.1	

Health Effects of OsO_4

Osmium tetroxide is already a highly toxic compound at very low concentrations. It is a rapid, indiscriminate oxidizer not distinguishing between organic tissue and inorganic materials. Inhalation, ingestion, and contact with skin and mucous membranes may result in severe consequences [2]. Most exposures to vapor are due to its high vapor pressure, which may cause severe chemical burns to the eyes, skin, and respiratory tract [3]. Short-term contact with the vapor may cause lacrimation accompanied by cough, headaches, and dizziness [4]. OsO_4 may cause irreversible blindness by turning the cornea black. Symptoms may not be noticeable until several hours after exposure, which may be an appealing feature for terrorists and make it difficult to detoxify [5]. Affected people may not realize immediately the extent of its toxic effects. Another delayed but severe effect following inhalation is acute lung injury, which may be followed by non-cardiogenic pulmonary edema [6]. Direct contact with a solution of osmium tetroxide will turn the skin black (severe chemical burns due to strong oxidizing properties) [7]. Painful burns or contact dermatitis may result, depending on the concentration. OsO_4 is not considered a carcinogen. Humans usually tolerate a maximum concentration of 0.1 ppm in air for 1.5 hours or 0.0001 ppm for 6 hours without harmful effects [8]. Osmium tetroxide does not have a medical antidote; therefore the treatment is supportive and symptomatic, depending on the route of exposure [9]. Initial treatment should focus on preventing further exposure. Victims should be removed from the contaminated area, undressed, and decontaminated by showering with water as soon as possible.

OsO_4 as a New Kind of Chemical Weapon and Possibility of Its Abuse

Physicochemical and health properties described above indicate that osmium tetroxide may be abused as a chemical weapon agent to contamine areas of human settlements.

A fundamental feature in this possibility is its volatility. Table 2 compares the saturation vapour pressures of water and select chemical war substances with osmium tetroxide. OsO_4 is highly volatile, even more than sarin, soman, substance VX – despite the fact that these are liquids. Solids and liquids with minimal evaporation do not cause a risk of intoxication by the inhalation route, unless they are converted by different mechanisms to aerosol. Thus, even liquid VX with low evaporation, which is still assigned to nerve agents with lethal effects on the nervous system, is considered to be a serious threat of intoxication of skin.

Relative vapor density of osmium tetroxide is also an important parameter, giving the number of times the vapor is heavier than air. This parameter makes it possible to express the behavior of the gas phase and aerosols and their vertical stability in the ground layer of atmosphere. The relative vapor density of OsO_4 is 8.78, while it is only 3.48 for phosgene. Osmium tetroxide will thus remain in the ground layer of the atmosphere, which will create conditions for human intoxication primarily by the inhalation route. Its smell will be easily detectable because, as we have already mentioned, it is characterized by a keen odor.

Compared with typical chemical warfare agents such as sarin, soman, phosgene, diphosgene, yperite, and others, osmium tetroxide has the closest properties to asphyxiating substances. Their common denominator is stifling effects and relatively low stability. Inhalation toxicity, long latency expression of clinical signs, and contamination of skin are comparable to yperite and lewisite.

LCt_{50} is a parameter that is often used to denote the vapor or aerosol exposure (Ct) necessary to cause death in 50% of the population exposed. The LCt_{50} value for OsO_4 is 1316 $mg \cdot min \cdot m^{-3}$, which is comparable to LCt_{50} of yperite, which is 1500 $mg \cdot min \cdot m^{-3}$. Comparison of toxicity of OsO_4 with some chemical warfare agents, which can intoxicate humans by the inhalation route, is shown in Fig. 1 [10-12].

Using osmium tetroxide as a chemical warfare agent is limited by the fact that OsO_4 is sold commercially in solid form bound to a polymer that is designed to eliminate the risk

of evaporation and increase the protection of workers, or an aqueous solution containing less than 6% OsO_4 because of limited solubility of this substance in water. Commercially marketed quantities are also very small and the prices are relatively high [13]. In spite of this, OsO_4 poses a serious threat as a possible tool for chemical terrorism, as evidenced by its inclusion in the list of potential toxic chemicals in the plans of terrorist attacks [3]. It is not suitable for an attack, especially for its relative rarity as well as not filling the bombs because of the strong oxidative properties. However, it could be used for a attack in enclosed areas with limited air circulation (airports, shopping centers) [6, 14].

Decontamination can reduce or completely eliminate the toxic action of osmium tetroxide. It is necessary to prevent the expansion of dust and fumes of osmium tetroxide in the ground layer of atmosphere. Then using respiratory and skin protection, OsO_4 must be removed in hermetically closed containers.

All contaminated clothing should be removed immediately and the contaminated person's skin should be washed thoroughly with soap and water. Excess water is a prerequisite for the elimination of toxicity arising from osmic acid. Eyes should be lavaged with copious amounts of normal saline or water for at least 15 minutes. OsO_4 solution can be decontaminated by exposure to excess vegetable oil because it contains mostly unsaturated bonds. Specifically, 10 ml 2% solution of OsO_4 is decontaminated by 20 ml vegetable oil, giving the products considered to be hazardous waste, or dried milk [12, 15].

Analysis

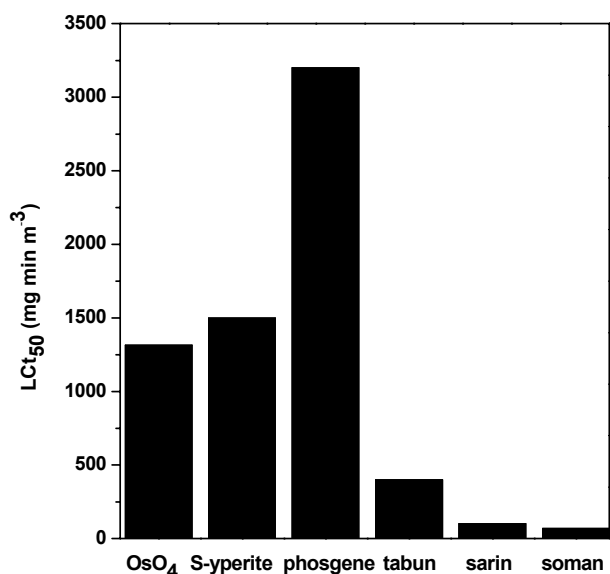From the preceding paragraphs it follows that osmium tetroxide is an important substance in the environment, and in analytical and biophysical chemistry. Therefore, detection of OsO_4 is essential. Many methods have been developed for determination of osmium tetroxide or osmium compounds utilizing osmium tetroxide as a chemical form or intermediate product in detection.

One of the oldest analytical methods, gravimetric analysis, uses distillation of OsO_4 in nitric acid or in a stream of chlorine for the determination of osmium. In this method, reduction of Os(VIII) to Os(IV) proceeds, followed by reduction to osmium metal, which is ignited and after drying and weighing osmium content is determined. The other direct gravimetric determination of osmium uses hydrazine hydrochloride as a reagent [16]. This method is effective, accurate, and reproducible, but it is too labor-consuming and normally makes the greatest contribution to the summary error of the analysis. The generally accepted gravimetric methods are those involving the reduction of osmium compounds to the metal.

Spectral Methods

In general, the 1960-90s saw a big growth in spectral and optical methods for determining osmium. One of the first methods was X-ray fluorescence, with a lot of benefits such as accuracy, non-destructiveness, and the ability to detect osmium without chemical extraction from biological samples. Also, this method is independent of the chemical state of osmium atoms.

It was observed that the reaction of OsO_4 with thiourea in acid medium gave a red combination of $[Os(thio)_6]Cl_3$ [17]. The results were not affected by systematic errors. The convenient, sensitive, reproducible, and accurate method for the spectrophotometric determination of osmium has been developed.

Other reagents have been used as complex-forming agents for the spectrophotometric determination of osmium in acid conditions, at room temperature and in maximum absorption [18-21]. Before determination, a stock solution of Os(VIII) was prepared by dissolving osmium tetroxide in very dilute sodium hydroxide, and then acidified by dilute hydrochloric acid to required pH. The availability, simplicity, and rapidity of the determination of osmium in a wide concentration range belongs to the advantages of spectrophotometric methods. Sawant in his work (Table 3) pointed out typical drawbacks of spectrophotometric determinations, such as narrow pH range, interference by many metal ions or instability of complexes at room temperature, their low molar absorptivity and photosensitivity [22].

It is often necessary to use appropriate separation and preconcentration technique [23]. The most commonly used are liquid-liquid extraction, solid-liquid extraction, or extraction into microcrystalline naphthalene (just by contact for a few seconds, the complex is separated by filtration, washed with water and dried) [24]. Multiple extraction is often used for increasing quantitative recovery of osmium [25]. Osmium is a rare metal in nature that occurs with platinum so their parallel spectrophotometric determination is very important. The sequential determination of osmium and platinum is based on the fact that reagent forms a com-

Fig. 1. Comparison of OsO_4 toxicity with some chemical warfare agents.

Table 3. The benefits and drawbacks of analytical techniques for the determination of Os (OsO$_4$).

Analytical method	Gravimetric analysis		Spectral analysis		Electrochemical analysis
	benefits	drawbacks	benefits	drawbacks	benefits
Determination of Os (OsO$_4$)	efficiency, accuracy, reproducibility, stability	labor-consumption, great summary error of analysis	accuracy, reproducibility, wide concentration range, availability, simplicity, rapidity	narrow pH range, interference by many metal ions, instability of complex, low molar absorptivity and photosensitivity, high equipment purchase, operational and maintenance costs	reproducibility, wide pH range, accuracy, low detection limit, linear dynamic range, low signal for background, no extraction and heating, low cost

plex with osmium at room temperature, and with platinum upon heating. There is no interference from platinum in the determination of osmium.

Quercetin, a flavonoid compound, was used as a chromogenic reagent for UV-VIS spectrophotometric methods for the determination of Os(VIII) (as OsO$_4$) and Os(IV) (as OsCl$_6^{2-}$ complex) in their mixtures. Quercetin does not react with the OsCl$_6^{2-}$ complex. The signals of the OsCl$_6^{2-}$ complex can be isolated from the examined mixtures by the calculation of the third-order derivative spectra [26].

Osmium tetroxide gives rise to very characteristic atomic emission properties. In acidic samples it gives much higher sensitivity than that given by the lower oxidation states (IV, III, II). However, in alkaline medium (pH=10.5) its atomic emission decreases, and the sensitivity is the same as that for the other oxidation states. It has been shown that there is a direct relationship between these characteristics of OsO$_4$ solutions and pH. With increasing pH the intensity of its atomic emission decreases. The volatility of OsO$_4$ has also been studied, and found to be minimal at around pH 9.5. This favours its determination at this pH [27]. Generally, the available spectrophotometric methods are not very sensitive, and few published methods have detection limits lower than 0.5 μg·ml^{-1}. Atomic absorption and atomic emission techniques offer poor detectability for osmium and are by no means free from interference.

Manzoori et al. [28] described a highly sensitive spectrophotometric method for the determination of trace amounts of Os(VIII) based on its catalytic effect on the oxidation of organic compounds, e.g. carminic acid (CA) by hydrogen peroxide (H$_2$O$_2$). Fig. 2 shows the absorption spectra of the CA-H$_2$O$_2$ system in the presence of osmium at different times. Owing to catalytic properties, osmium is usually determined by kinetic methods [29, 30]. They supply advantages such as high sensitivity, good selectivity, extremely low detection limit, needing only expediency operation, and simple equipment. However, many of these methods need strict control of catalytic reaction conditions, rigid control of acidity or reagent concentration, or are time consuming and have a high limit of detection. Their experimental conditions must be controlled exactly and repeatability is quite poor. Combining flow injection with a kinetic method, simple, economic, and rapid alternatives to other existing methods for determining Os(VIII) was developed.

The main features of these methods are high sampling frequency, low detection limit, good precision, low sample, and reagent consumption [31]. Xu et al. [32] applied a modified simplex method to the multivariable optimization of a new FIA system for determining micro amounts of osmium. A new, rapid, simple, and sensitive flow injection-kinetic method was developed. Osmium was distilled as OsO$_4$ and then completely reduced to Os (IV) by excess solid NaBH$_4$. The method has been proved to be adequate for the determination of osmium in a refined ore and a secondary alloy with satisfactory results.
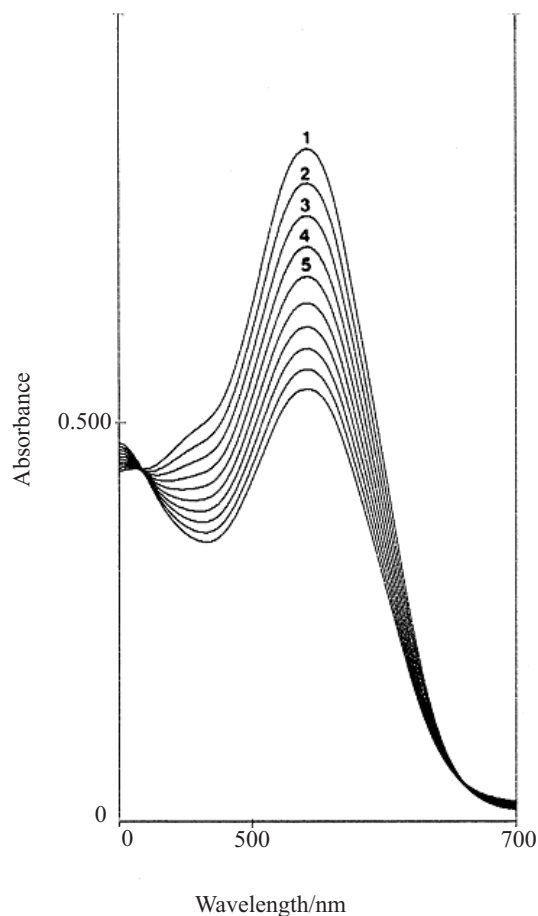

Fig. 2. Variation of CA-H$_2$O$_2$ oxidation system with time in the presence of Os(VIII); time interval for each scan 1 min. Conditions: CA, 1·10^{-4} mol·l^{-1}; H$_2$O$_2$, 0.013 mol·l^{-1}; Os(VIII), 1 ng·ml^{-1}; B$_4$O$_7^{2-}$, 2.5·10^{-3} mol·l^{-1}; pH 10; temperature 25ºC.

From the late 1970s, the determination of platinum group metals (mainly osmium) by ICP-AES was extensively investigated. Besides conventional nebulization, other sample introduction techniques like chemical vapor generation were also examined. It was shown that by injecting the osmium into the plasma as gaseous OsO_4, a sensitivity increase occurred along with other advantages [33]. In a more conventional field, such as flame atomic emission spectrometry (FAES), the preliminary extraction of osmium tetroxide in methylisobutylketone, followed by nebulization of the extract into a nitrous oxide-acetylene flame, provided a way to minimize interference [34].

Direct measurements of Os in water are critical in understanding the geochemical cycle of Os in the environment [35]. However, measurements of Os isotopes in natural waters are challenging due to the differences in oxidation states of naturally occurring and tracer Os that prevent accurate determination of Os concentration by isotope dilution. It has been recognized that the best way to chemically separate and purify Os and at the same time achieve tracer-sample equilibration is to oxidize Os in sample-tracer mixture to OsO_4. This method is an improvement over previous techniques because the time required to achieve complete oxidation is much shorter due to the increased temperature of reaction and the blanks are significantly lower due to smaller amounts of reagents used. A fast and simple method for the direct determination of low concentrations of Os and other platinum metals from the same sample aliquot by HR-ICP-MS has been developed by Pretorius [36]. Osmium is converted to its highest oxidation state, and forms highly toxic and volatile OsO_4 during the high-temperature oxidizing digestion process [37, 38]. Analyzing OsO_4 can result in a significant memory effect that impedes analysis time and requires extensive cleanup between analytical sessions [39]. Self-aspiration also avoids memory or contamination effects related to the use of peristaltic pump tubing.

For the investigation of geological and environmental materials, a highly selective analytical procedure for determining Ru, Rh, Pd, Re, Os, Ir, and Pt via isotope dilution were presented by Meisel et al. [40]. Sample preparation consists of a sample digestion step and drying down of the sample solution after the Os concentration was determined via sparging OsO_4 into an ICP-MS [41]. It can be demonstrated that a large portion of the higher standard deviations is caused by sample heterogeneity. Reproducibility (n=5) for Os was about 2% RSD.

Electrochemical Methods

Electrochemical techniques can advantageously be used to determine as well as to study the behaviour of platinum metals and its compounds. With respect to osmium, there are also some contributions that describe the use of classical polarography, voltammetry, or coulometry for such purposes. Linear sweep voltammetric and square wave voltammetric techniques on a hanging mercury drop electrode were proposed for determining ultratrace amounts Os(VIII) using a catalytic wave of OsO_4-bromate system by Ensafi and Zarei [42]. Under optimized conditions, the linear sweep voltammetric procedure gives excellent reproducibility, limits of detection, linear dynamic range, and low signal of background, while the square wave voltammetric technique gives higher sensitivity, but the background signal was high and the linear dynamic range was narrower. The methods are suitable for the determination of osmium as osmium tetroxide as low as $5 \cdot 10^{-10}$ mol·l^{-1}. The effect of possible interference is easily removed by a single extraction of osmium into methyl isobutyl ketone. A rapid potentiometric method was proposed by Zaky et al. [43]. The method is based on the addition of arsenite to Os(VIII) to reduce it to the metallic state. The excess of arsenite was oxidized by iodine dissolved in acetic acid. The liberated iodide was then potentiometrically titrated against mercury(II) using silver amalgam as the indicator electrode. Some binary and ternary mixtures were completely analyzed. Amin and Saleh described a simple, rapid, and accurate potentiometric method for the determination of Os(VIII) in the concentration range 0.4-4.0 mg·ml^{-1} [44]. Hydrazine hydrochloride was added to Os(VIII) to reduce it to Os (IV). The excess of hydrazine hydrochloride was oxidized by iodine dissolved in acetic acid. Similar to the previous case, the liberated iodide was potentiometrically titrated using silver amalgam as the indicator electrode. The relative standard deviation for six replicate determinations of Os(VIII) in binary and ternary mixtures is determined without the need for extraction or heating.

The rate of reaction between arsenite and vanadate catalyzed by Os(VIII) was monitored using an automatic potentiostatic stat method [45]. This was carried out by maintaining the preset potential of a platinum indicator electrode by addition of a vanadate solution as titrant. The method is sensitive enough to determine trace osmium and superior in terms of selectivity and indifference to the spectrophotometric monitoring problems such as absorptivity of the substance measured, absorption interference from other components of working solution, or use of special spectrophotometer, appropriate optical sensor, and transducer. The limit of detection of osmium was $3 \cdot 10^{-8}$ mol·l^{-1}.

The benefits and drawbacks of gravimetric and spectral methods for determination of Os (OsO_4) are mentioned in Table 3.

Conclusions

In the proposed work we described the properties of osmium tetroxide. It is a toxic substance with high evaporation, which may be the cause of the use of OsO_4 as a chemical warfare agent with asphyxiating effect. Since its smell will be easily detectable, it may be abused in objects with high human concentration in enclosed areas with limited air circulation (airports, shopping centers). Some analytical techniques for the determination of osmium (OsO_4) in various matrixes are described here.

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