

Monitoring of V(IV) and V(V) in Etnean drinking-water distribution systems by solid phase extraction and electrothermal atomic absorption spectrometry

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Abstract

Monitoring activities carried out since 1994 showed the presence of significant levels of vanadium in drinking waters delivered in a lot of Etnean towns. The highest vanadium concentration was found in ground waters collected in the drainage gallery Ciapparazzo located on the Northwestern flank of Mt. Etna in Bronte's area (Catania, Italy). This drainage gallery, with a flow rate of near 5001 s^{-1} , is an important water source for several towns of the Etnean province. On account of different toxicological behaviours of V(IV) and V(V), which are the only possible oxidation states in aqueous media, a research project was set up to evaluate the ratio between their concentrations before and after disinfection treatments (chlorination or UV irradiation). Data were acquired in the most representative sites of the drainage gallery and the distribution network to evaluate the effect of residence times and disinfection treatments on possible species interconversion. The average total concentration of vanadium was $165 \mu\text{g l}^{-1}$. Speciation analyses performed by solid phase extraction of both species followed by furnace atomic absorption spectrometric determination of V(IV) eluates revealed that the latter was the predominant species (90–100%) in untreated waters. Moreover, among the two disinfecting treatments applied by the water supplier, only sodium hypochlorite altered the species ratio and determined an instant increase of near 20% in V(V) relative concentration. No significant effect was observed as residence time varied in the drainage gallery or in the distribution systems. Other physico-chemical and chemical parameters (i.e. pH, E_H , water temperature, electrical conductance, dissolved oxygen as well as major and minor inorganic cations and anions) were determined in the collected water samples to evaluate if they are proper or not for interconversion of the two V species. Redox potential of the water was also correlated to the percentage of V(IV).

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1. Introduction

Vanadium is a trace element of ubiquitous distribution that constitutes about 0.02% of the Earth's crust. It can exist in many oxidation states from -1 to $+5$ and in a number of oxyanionic and oxycationic forms [1,2]. The multiple oxidation states, ready hydrolysis and polymerization confer a level of complexity to its chemistry well above that of many other transition metals. Vanadium dissolves in natural waters as vanadyl and vanadate ions [3]. The coexistence of these species depends on pH, redox potential and ionic strength of the aqueous system [4–7].

Food is the main source of exposure for general population with an estimated daily dietary intake of 10–63 μg [8]. Vanadium

concentration in ground and surface waters is largely dependent on geographical location; typical values range from 1 to $6 \mu\text{g l}^{-1}$ in unpolluted areas [9,10]. Therefore, drinking water contribution to V ingestion is generally negligible except where relative high concentrations of the element (usually $40\text{--}100 \mu\text{g l}^{-1}$) have been recorded mainly as an effect of the presence of volcanic rocks [9,10].

Vanadium at levels observed in seawaters ($0.2\text{--}29 \mu\text{g l}^{-1}$) was shown to be an essential element for normal cell growth of some lower organisms [11–13]. Although no specific functional role has been discovered in higher animals [14], its salts can interact with a number of enzymatic systems. As a consequence of these interactions, it is capable of sustaining diverse physiological activities ranging from antitumorogenicity [15–20], mitogenicity [21–24], and inhibition of key metabolic enzymes such as phosphoglucosyltransferases and others [25–27]. It is generally known to have insulin-mimetic activity demonstrated

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Table 1
Synopsis of the monitoring activity

Campaign	Period	Monitored area	No. of sampling sites	Disinfection treatment
I	Apr 2003	Drainage gallery	6	none
II	Jul 2003	Drainage gallery	7	none
II	Jul 2003	Minor and main pipelines from Ciapparazzo to Adrano	7	temporary suspended
II	Jul 2003	Main pipeline from Ciapparazzo to Adrano	2	NaOCl
II	Jul 2003	Minor pipeline from Ciapparazzo to Adrano	5	UV
III	Oct 2003	Main pipeline from Ciapparazzo to Belpasso	4	temporary suspended
III	Oct 2003	Main pipeline from Ciapparazzo to Belpasso	4	NaOCl

both in animal models and in clinical studies on a limited number of diabetic subjects [28–37]. However, numerous reports have warned of the carcinogenic and other toxic effects of vanadium when present at higher concentrations [38–54]. Even though toxicological studies are not yet exhaustive, it is generally recognized that its biological action depends on its oxidation state [55] and that V(V) is more toxic than V(IV) [56–59]. Therefore, it is essential to determine the accurate concentration of the two species in environmental and biological samples for a better understanding of the overall toxicity of the element.

Monitoring activities carried out since 1994 on Mt. Etna's surface (Sicily, Italy) showed the presence of significant levels (much greater than $50\mu\text{g l}^{-1}$) of vanadium in ground waters collected from the foothill area between 500 and 1000m above sea level [5,60,61]. The highest vanadium concentration ($160\text{--}220\mu\text{g l}^{-1}$) was found in the drainage gallery Ciapparazzo located on the Northwestern flank of the volcanic edifice near the municipality of Bronte (Catania, Italy). This drainage gallery is an important irreplaceable water source for several towns of the Etnean province since it secures a water flow rate of near 500 l s^{-1} .

On account of the different toxicological behaviour of V(IV) and V(V), a research project was set up to evaluate the ratio between their concentrations before and after disinfection treatments (chlorination or UV irradiation). Acquired data

allowed evaluating the effect of residence time and disinfection treatment on possible species interconversion. In this article we discuss results obtained from the fractional determination of the two species in samples collected in the most representative sites of the drainage gallery and the distribution network.

2. Experimental

2.1. Drinking water network and sampling area

In this study water samples were collected from the first part of the distribution network administrated by *Azienda Consortile Servizi Etnei* (A.Co.S.Et., Catania, Italy), which is the most important water supplier in the Etnean area. This public consortium distributes drinking water to the twenty associated municipalities located in the western and southern foothill area of Mt. Etna. A.Co.S.Et. collects ground waters from the spring Maniace ($60\text{--}110\text{ l s}^{-1}$), the drainage gallery Ciapparazzo (450 l s^{-1}), the wells Sacro Cuore and Magri (80 l s^{-1} each) and other minor private wells. The most important contribution comes from the drainage gallery Ciapparazzo, which is situated just in the area where high levels of vanadium were found [5,60,61]. At the exit of the drainage gallery, a small fraction of the water flow (about 20%) is irradiated with UV light and distributed in the surroundings with a minor pipeline (400mm wide). The remaining 80% of the water is chlorinated by adding

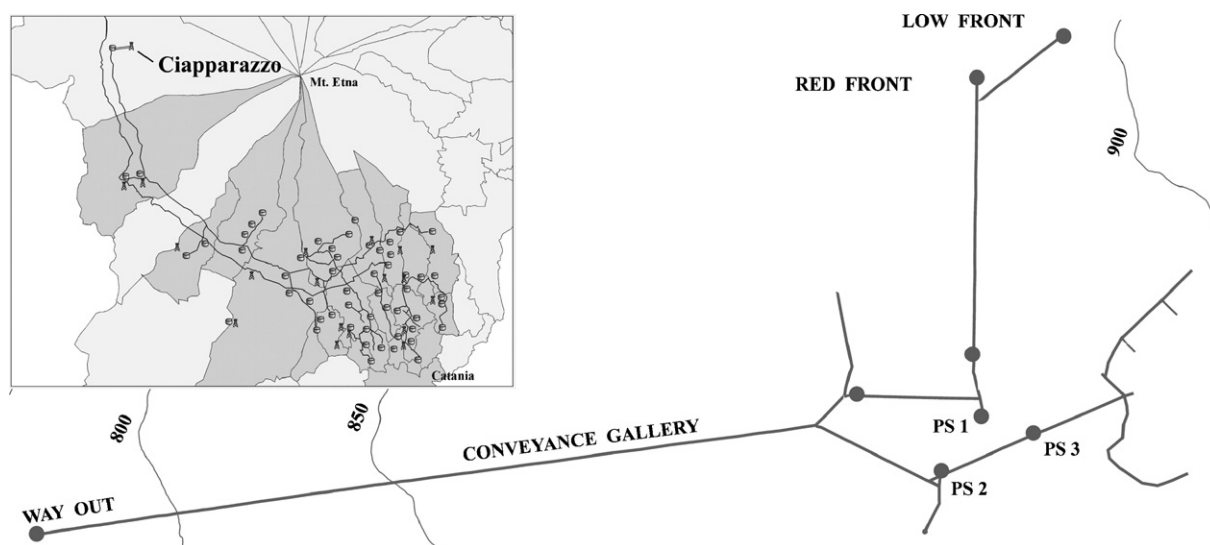


Fig. 1. Detailed map of the drainage gallery Ciapparazzo (Sicily, Italy). Circular marks represent the sampling sites. PS: pumping station.

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