



Analysis of Extended Ultra-trace Nitrosamines in Drinking, Recycled & Catchment Water

INTRODUCTION

Nitrosamines are a group of potential contaminants typically resulting from chlorination or chloramination of water or waste water. Nitrosamines found in drinking waters can be formed through several pathways, including when residual disinfectants such as chlorine or chloramine react with amines. Sources of nitrosamine precursors may include algal or wastewater affected source water, cationic polymers, anion exchange resins used in water treatment and natural organic matter (NOM)^[2]. The production of NDMA in recycling waste water for drinking water supplies is therefore of particular interest to stakeholders.

Global studies have identified the nitrosamine compound N-Nitrosodimethylamine (NDMA) as a potential chemical of concern in the environment. This increased interest in NDMA and other nitrosamines has lead ALS to complete a second research & development project which now provides **NATA Accredited testing for an extended range of Nitrosamine compounds** to Limits of Reporting (LOR) as low as 0.003 µg/L or three parts per trillion (ppt).

NDMA – PROPERTIES AND USES

NDMA is a semi-volatile organic chemical of the nitrosamine group that is highly toxic, extremely soluble in water, is an industrial by-product and a probable human carcinogen. NDMA is used as an industrial solvent, an anti-oxidant, a rubber accelerator and in the preparation of polymers where it may be used as an initiator or plasticizer. The compound has been used in the production of rocket fuel, as biocide for nematodes and an intermediate for 1,1-dimethylhydrazine to inhibit nitrification of soils.^[1]

METHOD INFORMATION

ALS METHOD CODE

EP239 & EP239B (NDBA only), EP232 (NDMA only)

LIMITS OF REPORTING (LOR)

Drinking Water: 0.003 - 0.02µg/L

METHOD REFERENCE

US EPA Method 521

HEALTH CONSIDERATIONS

NDMA first came to attention as a groundwater contaminant in California in 1998 at several sites that produced rocket fuel.

Nitrosamines, mainly NDMA, NMEA and NDEA are highly mutagenic compounds that are suspected of carcinogenic activity to the human body. NDMA is carcinogenic in experimental animals through several exposure routes, including ingestion in drinking water. In 1987 the International Agency for Research on Cancer (IARC) classified NDMA as a Group 2A chemical, probably carcinogenic to humans. NDMA (CAS# 62-75-9) is highly toxic and is a documented hepatotoxin that can cause liver tumours in rats at very low doses.

NDMA's contamination of drinking water is of particular concern due to the minute concentrations at which it may harmful, the difficulty in detecting it at these concentrations and to the difficulty in removing it from drinking water. It should also be considered that NDMA levels in drinking water may be an indicator of the presence of structurally related compounds, some of which may also have carcinogenic properties.

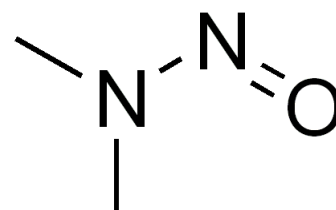
REGULATORY GUIDELINES

The Australian Drinking Water Guidelines 2011 (ADWG) and Australian Guidelines for Water Recycling 2008 (AGWR) have both established maximum allowable concentrations for NDMA and NDEA which may be present in drinking or supply augmentation water. The California Department of Public Health (CDPH), the location of the first major NDMA detection, has set notification levels for three nitrosamine compounds. The current published guideline concentrations for various nitrosamines are detailed below.

Analyte	ADWG 2011 (µg/L)	AGWR 2008 (ng/L)	CDPH 2011 (ng/L)
NDMA	0.1	10	10
NDEA	N/A	10	10
NDPA	N/A	N/A	10

ANALYSIS OF NITROSAMINES

ALS methodology is based upon USEPA Method 521 version 1.0 September, 2004^[3]. ALS substitutes the more sensitive tandem LC-MS-MS finish in place of the gas chromatography-chemical ionisation-mass spectrometry used in the original method. The ALS method has a detection limit (MDL) of less than 0.001 µg/L (1ppt) for common matrices, and therefore the degree of confidence at the standard LOR of 0.003 µg/L is very high. Table One below summarises the nitrosamine compounds analysed and the respective LOR.



NDMA

Table One: Nitrosamine Compounds Included in ALS Method EP239 & EP239B

Abbreviation	Compounds	CAS Number	LOR (µg/L)
NDMA	N-Nitrosodimethylamine	62-75-9	0.003
NMEA	N-Nitrosomethylethylamine	10595-95-6	0.003
NDEA	N-Nitrosodiethylamine	55-18-5	0.01
NDPA	N-Nitrosodi-n-propylamine	621-64-7	0.003
NDBA	N-Nitrosodi-n-butylamine	924-16-3	0.02
NPip	1-Nitrosopiperidine	100-75-4	0.003
NMor	Nitrosomorpholine	59-89-2	0.003
NPyr	1-Nitrosopyrrolidine	930-55-2	0.01

Due to the slight structural variation of NDBA, this compound needs to be analysed via a separate method (EP239B).

LIMITING NDMA FORMATION

Reducing the occurrence of NDMA in drinking water systems may conflict with the goals of maintaining a persistent chlorine residual in distributions and controlling levels of other disinfection by-products such as trihalomethanes and haloacetic acids. The potential for NDMA formation may be reduced by avoiding chloramination through the removal of ammonia prior to disinfection, or by operating the system for breakpoint chlorination.^[1]

GENERAL SAMPLING & PRESERVATION REQUIREMENTS

Drinking Water: 2 x 500mL Amber Glass Bottle preserved with Sodium Thiosulphate.

Storage: stored at 4°C.

Holding Time: Extract within 7 days, Analyse within 40 days.

For further information please contact your local ALS Client Services team.

REFERENCES

^[1] National Health Medical Research Council, Australian Drinking Water Guidelines 6 2011.

^[2] American Water Works Association – Opflow, Nitrosamines: Economics of the Unknown, June 2011.

^[3] 13.1 US EPA Method 521, Determination of Nitrosamines in Drinking Water by Solid Phase Extraction and Capillary Column Gas Chromatography with Large Volume Injection and Chemical Ionization Tandem Mass Spectrometry, Version 1.0, 2004.