

# Preliminary Performance Evaluation of the Gold Nanoparticle Method for Quantification of Residual Poly-(Diallyldimethyl Ammonium Chloride) in Treated Waters in the Umgeni Water Catchment, Kwazulu-Natal (South Africa)

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## Abstract

A "real world" study to assess the performance characteristics (precision, accuracy) of the citrate-capped, gold nanoparticle, Ultraviolet-Visible colorimetric method, for quantifying residual poly-diallyl dimethylammonium chloride (poly-DADMAC) in four raw dam and treated potable waters, was undertaken. Using three calibration methods, the method was found to be sensitive (LOQ=2 µg/L), over the linear range 10-30 µg/L. The overall mean within-batch precision (%RSD) was: 7.42 (±7.07) for Method 1, and 7.66 (±7.37) for Method 2; between-batch (reproducibility) (%RSD) was 54.37 ± 30.03 and 35.89 ± 34.89). Statistical data analysis indicated fairly good agreement (no significant difference) for poly-DADMAC levels in 30 samples analyzed by the two methods Method 1 and 2. The residual poly-DADMAC potable water levels (range: <2-8 µg/L), were: on average (±SD) (µg/L), 1.21 (±1.31) for Hazelmere Dam, 1.22 (±0.55) for Midmar Dam, 3.40 ± 3.89) for Inanda Dam, and 3.64 (±3.83) for Nagel Dam. The observed, apparent poly-DADMAC levels, obtained by Method 1, (range: 6-16 µg/L) were, on average (±SD) (µg/L), for the raw water samples: 3.73 (±0.46) for Inanda Dam, 5.73 (±6.57) for Nagle Dam, 6.82 (±9.03) for Hazelmere Dam and 10.12 (±6.94) for Midmar Dam. The study indicated compliance of all treated, potable water for residual poly-DADMAC, to the current international limit of ≤50 µg/L. The relatively high apparent concentration (range: <2-24 µg/L) of poly-DADMAC observed on the raw dam waters was attributed to the presence of Natural Organic Matter (NOM).

**Keywords:** Citrate-capped gold nanoparticle; Water treatment polymer; Poly-(diallyldimethylammonium chloride); Residual polyelectrolyte; Colorimetry; Ultraviolet-visible spectroscopy; Natural organic matter; Disinfection by-product; Toxicity; N-nitrosodimethylamine

## Introduction

Poly-diallyldimethylammonium chloride (poly-DADMAC) is one of the most commonly used organic polyelectrolytes in wastewater and potable water treatment plants, as a coagulant and as a flocculent aid, for floc formation and for improved settling of larger particles [1-5]. Due to its potential to form N-nitrosodimethylamine (NDMA) [6-8], there has been, in recent years, a growing concern over the fate of poly-DADMAC within the water treatment process. Some early work has demonstrated that NDMA is a disinfection by-product formed during chlorination steps within the water treatment process [9].

Furthermore, NDMA is a suspected carcinogen [1,6,8,10,11]. The presence of residual poly-DADMAC depends on its reactivity during the disinfection processes, and whether it degrades into toxic compounds, or other by-products, that pass through the various stages in the water treatment process. Due to the highly charged nature the main assumption is that it will be removed together with the sludge during flocculation in the water treatment process.

Personal care products are another source of polyelectrolytes that can enter the environment and water treatment facilities, where they may not be adequately removed in the water treatment process [12,13]. Residual amounts may persist if the incorrect dose is used. The American Water Works Association (AWWA), American Society for Testing Materials, The European Committee for Standardization, the National Sanitation Foundation International, and the American

National Standards Institute, provide standards for the maximum dosage of polyelectrolytes (10-100 mg/L) that can be used in water treatment. They have set the residual amount of poly-DADMAC in drinking water at 50 µg/L [3,14,15]. Recent work has shown that polyelectrolytes, like poly-DADMAC, can be toxic to aquatic organisms at levels above 50 µg/L [12,13].

Thus, for water treatment plants using poly-DADMAC as coagulant, and from an environmental, human health perspective, there is a strong requirement to determine the amount of residual polyelectrolytes, like poly-DADMAC, in the drinking water. To monitor residual concentrations in water, down to the required limit of ≤50 µg/L, sensitive analytical methods are therefore required.

Colloid titration has been used to determine residual poly-DADMAC in water samples [1,2,16]. However, the sensitivity of such

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techniques is 0.5-1.0 mg/L. The AWWA standard for poly-DADMAC [17] uses a gravimetric method; the method is long, labor-intensive and cannot be applied to analysis of residues in treated water. The other challenge is that the cationic polymer is ultraviolet (UV) inactive, and it is therefore not possible to employ UV-Visible (Vis) spectrophotometry for its analysis [18,19]. Pre- and post-fluorescent tagging of poly-DADMAC, with 10-40 µg/L detection limits in water, was developed by Elridge [4]. However, these methods are complicated, require several pre-treatment steps, can be expensive, are very time-consuming, and may not be suitable for routine analysis. A novel gel permeation chromatography (GPC) method, using RI detection, was developed by W John [18,19], for poly-DADMAC analysis in water, with a detection limit of 50 mg/L, and 1% precision. A spectrophotometric detection method, of poly-DADMAC, exploiting the flocculation properties using 4-hydroxy-1-naphthylazo-benzene-sulfonic acid, which forms a coloured colloid ion pair, was reported by Ndungu et al. [20]. The method had a linear range of 0.1-1.8 mg/L, with a limit of detection (LOD) of 0.07 mg/L.

Umgeni Water, a bulk potable water supplier, in KwaZulu-Natal (KZN), makes use of this organic polymeric poly-DADMAC as a coagulant in some of its water treatment plants. However, to date the residual amount of poly-DADMAC in the final drinking water from any of the plants using poly-DADMAC, has not been fully investigated or accurately determined. Although we have a state-of-art water testing laboratory at the head office in Pietermaritzburg (KZN), which is ISO/IEC 17025-accredited, and beside the earlier work on analytical method development for quantification of residual poly-DADMAC [2,18,19], there are no automated, rapid, simple "in-house" test methods available, at national, and international, level, for accurate, low level, residual poly-DADMAC analysis in water.

Gumbi et al. [21], from the University of KwaZulu-Natal (South Africa), developed a novel, sensitive spectroscopic technique for poly-DADMAC analysis, using citrate-capped gold nanoparticles (Au-NPs), which was applied to analysis of river water samples, with a reported 1-100 µg/L detection range [21]. We hypothesized that this newly developed gold-nanoparticle analytical method would be suitable for the accurate, precise low level quantification ( $\leq 50$  µg/L) of residual poly-DADMAC in treated water. The aim of this study was thus: to evaluate the suitability of the recently reported gold-nanoparticle method [21] for determination of residual poly-DADMAC in typical/real potable, water samples treated with polyelectrolyte-based coagulant: poly-DADMAC; to assess the precision and accuracy of this analytical test method.

We now report on the preliminary performance of this analytical test method. To our knowledge, this is the first report of a "real world" study application of the citrate-capped, Au-NP colorimetric method for quantitation of residual poly-DADMAC in treated, and raw, dam water for potable use.

## Materials and Methodology

### Reagents and chemicals

The three organic polyelectrolyte-based coagulants, containing poly-DADMAC, (with the water works at which it is used) were: Z553D (DV Harris, Wiggins), obtained from Zetchem (KwaZulu-Natal, South Africa); SF3456 (Hazelmere water works) and SF3435 (Durban Heights), were obtained from Improchem (KwaZulu-Natal). The composition of the coagulant blends (Aluminium chlorhydrin-DADMAC) was unknown due to it being proprietary information.

The Acrodisc premium 25 mm syringe filter with GxP/0.45 µm GHP membrane (HPLC certified - Glass fiber prefilter (GHP: hydrophilic polypropylene, Part Number: AP-4559T) was obtained from Pall life Sciences. Gold (III) chloride tri-hydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ), tri-sodium citrate (99%) ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ ) and poly diallyl dimethyl ammonium chloride (poly-DADMAC) 35% weight (average molecular weight 100,000) ( $\text{C}_6\text{H}_{16}\text{ClN}$ ) were obtained from Sigma Aldrich and were of analytical grade. All chemicals were used without further purification. All glassware used was salinized to prevent the adsorption of poly-DADMAC and other charged species. Plastic containers were used to store all solutions.

### Instrumentation for poly-(DADMAC) analysis

The Ultraviolet (UV)-Visible (Vis) spectra were measured with an Ocean Optics spectrometer (model HR2000+), equipped with a tungsten halogen (Ocean Optics) based module, and two fiber optic cables (QP 600-2-vis-BX model 727-733-2447, suitable for 400-2100 nm range, from Narich Ltd (Milnerton, South Africa, agents for Ocean Optics); raw data were captured and analyzed with the spectrometer SpectroSuite<sup>®</sup> software. Samples were transferred to a 1.0 ml quartz cuvette and placed in the cuvette holder (Ocean Optics CUV-UV with a 1 cm path length). The light was passed through a fiber optic cable, then the cuvette holder and finally via a second fiber optic cable to the spectrometer.

### Instrumentation for physical tests

For the 51 study samples, the pH, salinity, conductivity, Redox, TDS and temperature, were determined at UKZN. The Redox and pH were measured with an 827 pH lab meter equipped with a probe (6.0220.100) bought from Metrohm (Switzerland). Salinity, conductivity and total dissolved solids (TDS) were measured with an InoLab<sup>®</sup> Cond level 1 (8F93) instrument, equipped with a probe (WTW Tetracon 325), bought from Germany, through Merck. Both probes were conditioned with standards (as per the manufacturer's recommendations) before use every day. Similar physical tests were performed at the Umgeni Water Chemistry laboratory. Turbidity, in Nephelometric Turbidity Units (NTU), was measured with a HACH 2100 turbidimeter. The total organic carbon (TOC) was measured with a Tekmar Torch analyser, from LabHouse (Midrand, South Africa), agents for Tekmar. The total dissolved solids (TDS) were determined by gravimetry. A JOEL 1010 transmission electron microscope was used for transmission electron microscopy (TEM) analysis of the gold nanoparticles [20]. Samples were initially prepared by dipping a 200 mesh copper grid (Formvar support film) in the sample solution, air-drying on filter paper, followed by TEM analysis.

### Preparation of stock solution of gold nanoparticles

As per the previous report [21], Au-NPs were prepared by the citrate reduction method [22]. Gold(III) chloride tri-hydrate (0.4768 g) was added to 400 ml of ultrapure water. The gold solution was then heated on a hotplate, 10 ml of 0.2746M tri-sodium citrate was added to the boiling gold solution. The solution was stirred (300 rpm) and carefully observed for the color change, from yellow to colorless and finally to deep red. The red solution was immediately taken off the hotplate and allowed to cool to 25°C. The Au-NP solution (400 ml) was then transferred to a 2.0 L volumetric flask, and diluted with ultrapure water to volume. The solution was thoroughly mixed by inverting the flask for 20 times; no precipitate was observed. The Au-NPs were characterized by UV-Vis spectroscopy and TEM.

## Jar test procedure

The purpose of Jar tests are used to predict clarification at water works. This method may be used to determine optimum dose of a polyelectrolyte for use as a primary coagulant and for comparing the performance of different polyelectrolytes. The Jar tests were performed at Wiggins Water Works, Umgeni Water. The standard procedure [23] is described in the Supplementary Material Text A. The optimum dose and most suitable coagulant for a particular site can be deduced from the Jar test results.

## Sample collection

The four selected raw water sources (dams) (and respective water works (WW)) were: Inanda Dam (Wiggins WW), Nagle Dam (Durban Heights WW), Hazelmere Dam (Hazelmere WW) and Midmar Dam (DV Harris WW). Grab, raw water samples, and treated water samples, were collected from the designated water works sampling points that each dam supplies; each sample site has a unique sample point code. Samples were collected into 1 L plastic bottles, during the three-month study period: May, June and July 2014. The raw, potable (treated) water, and processed samples from the Jar Test procedure, were then submitted, in 1 L plastic bottles, to UKZN for subsequent analysis for poly-DADMAC. All collected and processed samples were assigned a unique identification number; the composition of the samples was not disclosed to the testing laboratory (UKZN) for the purpose of establishing accuracy and precision of the analytical method for residual poly-DADMAC.

## Determination of poly-DADMAC by colorimetry-Au-NP

Poly-DADMAC in the various water samples were analysed by the standard addition method [21]. The UV-Vis data obtained on each water sample was analysed by using three techniques: Absorbance of the peak at 690 nm (Method 1) (M1), Area of the peak at 690 nm (Method 2) (M2), and Ratio of the peak absorbances at 690 nm and 520 nm ( $A_{690\text{nm}}/A_{520\text{nm}}$ ) (Method 3) (M3).

**Calibration standards:** All glassware was silanized before use. A 1.185 g sample of poly-DADMAC (35% weight) was weighed into a vial (plastic) and transferred into a 1 L volumetric flask to make a 400 mg/L of poly-DADMAC stock solution. A 50 mg/L working stock

solution of poly-DADMAC was prepared by transferring 12.5 ml of poly-DADMAC stock solution (400 mg/L) into a 100 mL volumetric flask. All flasks were then diluted to volume with double distilled water. Three calibration standards: 0, 10 and 20 µg/L, in 50 ml flasks, were used for Method 1 and Method 2; for Method 3, the 3 calibration standards were between 10-50 µg/L.

**Determination of poly-DADMAC by colorimetry-Au-NP:** The real water samples were initially filtered through the 0.45 µm GHP pre-filter membrane. Approximately 25 ml of ultrapure water (or water sample) was added into a 50 ml volumetric flask. For the calibration standards, the required amount (e.g., 10 µL for a 50 µg/L standard) of a 50 mg/L poly-DADMAC solution was added to the contents of the flask. A volume of 20 ml of the Au-NP solution was then added to the flask. The blue solution was made up the 50 mL mark, mixed (by inverting the flask 20 times) and analyzed within 20 minutes. This was done to avoid the coagulant effect of poly-DADMAC.

## Statistical data analysis

The comparison of observed poly-DADMAC levels for each sample determined by all three calibration methods were determined by one-way analysis of variance, and Bonferroni adjustment was performed afterwards to investigate significant pairwise differences. Tests for correlation and significance (p-values less than 5%) were determined using STATA12, by analysis of Scatter plots and determination of Pearson's correlation coefficient.

## Other Physico-chemical water quality data

Other physico-chemical data, like TOC and turbidity, were, as required, obtained from the Umgeni Water Intranet, via the Labware Information Management System (LIMS).

## Results

### Physico-chemical water quality

After data analysis, the average turbidity, conductivity, TDS and TOC values are summarized in Table 1. The raw data is appended in the Electronic Supplementary Material Table A, Figures A and B.

For the 3-month study period, the average raw water turbidity

Dam (raw water source)	Water works: Raw water Sample point	Raw WW <sup>b</sup> point supplied by dam					Water quality of the 51 study samples				Potable water source		
		n	Turb <sup>b</sup> NTU <sup>b</sup> Mean (±SD) (NTU)	Turb NTU% RSD	Turb NTU Range (NTU)	TOC <sup>b</sup> Mean (±SD) (mg/L) (%RSD)	Con <sup>b</sup>	Con	TDS <sup>b</sup>	TDS	WW sample point	(NTU) Mean ± SD (%RSD)	TOC Mean ± SD (mg/L) (%RSD)
Inanda	Wiggins: TWG001 (0.08-1.01) <sup>a</sup>	92	1.04 (±0.30)	28.60	0.50-1.99	2.59 ± 0.20 (7.81)	197.5 ± 65 (32.92)	229.8 ± 5 (24.52)	232.4 ± 12.1 (0.05)	251.2 ± 29.4 (11.71)	TWG010	0.26 ± 0.08 (32.10)	2.33 ± 0.27 (11.67)
Nagel	Durban Heights: TDH001 (2.4)	92	4.96 (±2.12)	42.70	2.11-14.80	2.31 ± 0.12 (5.07)	73.7 ± 23.2 (31.55)	95 ± 50.9 (53.59)	123.2 ± 22 (17.87)	128.5 ± 15.9 (12.39)	TDH010	0.22 ± 0.06 (28.15)	2.16 ± 0.26 (12.20)
Hazelmere	Hazelmere: THM001 (2-5)	92	6.71 (±1.54)	22.92	4.00-14.50	2.48 ± 0.25 (9.96)	112 ± 62.2 (55.56)	159.3 ± 30.1 (18.87)	151.4 ± 11.4 (7.52)	208.5 ± 75.1 (36.04)	THM008	0.66 ± 0.21 (32.46)	1.91 ± 0.35 (18.17)
Midmar	DV Harris: TMM001 (1.63-5)	92	9.38 (±4.54)	48.46	0.90-43.10	3.17 ± 0.62 (19.44)	59.3 ± 23.7 (39.93)	77 ± 33.2 (43.05)	70.3 ± 5 (7.13)	90.4 ± 8.5 (9.37)	TMM007	0.25 ± 0.07 (28.08)	2.04 ± 0.39 (19.14)

<sup>a</sup>Coagulant dosing level (mg/L)

<sup>b</sup>Con: Conductivity; TOC: Total Organic Carbon; TDS: Total Dissolved Solids; Turb: Turbidity; NTU: Nephelometric Turbidity Units; WW: Water Works.

Table 1: Physico-chemical water quality data.

(NTU) ( $\pm$ Standard Deviation (SD)) was: 1.04 ( $\pm$ 0.30) for Inanda, 4.936 ( $\pm$ 2.12) for Nagle, 6.71 ( $\pm$ 1.54) for Hazelmere and 9.38 ( $\pm$ 4.54) for Midmar. For the conductivity, the average levels (mS/m) were: 59.3 ( $\pm$ 23.7) for Midmar, 73.7 ( $\pm$ 23.2) for Nagle, 112.0 ( $\pm$ 62.2) for Hazelmere and 197.5 ( $\pm$ 65) for Inanda. The average TDS levels (mg/L) were: 70.3 ( $\pm$ 5) for Midmar, 123.2 ( $\pm$ 22) for Nagle, 151.4 ( $\pm$ 11.4) for Hazelmere and 232.4 ( $\pm$ 12.1) for Inanda. The average TOC levels (mg/L) were: 2.31 ( $\pm$ 0.12) for Nagle, 2.48 ( $\pm$ 0.25) for Hazelmere, 2.59 ( $\pm$ 0.2) for Inanda and 3.17 ( $\pm$ 0.62) for Midmar. The overall Redox potential values (mV) were (mean  $\pm$  SD) (median) (range): -30  $\pm$  (29) (-25) (range=+7 to -80) for all four dams. Individual average values were: -41  $\pm$  (49) (-41) (-76 to -6) for Midmar, -32  $\pm$  (43) (-25) (-79 to 7) for Hazelmere, -25  $\pm$  (1) (-25) (-25 to -24) for Nagle, -20  $\pm$  (18) (-27) (-34 to 12) for Inanda. The average values for pH were (mean  $\pm$  SD): 6.82 ( $\pm$ 0.37) for Inanda, 7.09 ( $\pm$ 0.16) for Nagle, 7.15 ( $\pm$ 0.66) for Hazelmere and 7.17 ( $\pm$ 0.6) for Midmar.

For the potable water, the average raw water turbidity (NTU) was: 0.22 ( $\pm$ 0.06) for Nagle, 0.25 ( $\pm$ 0.07) for Midmar, 0.26 ( $\pm$ 0.08) for Inanda and 0.66 ( $\pm$ 0.21) for Hazelmere. For conductivity, the average levels (mS/m) were: 77 ( $\pm$ 33.2) for Midmar, 95.0 ( $\pm$ 50.9) for Nagle, 159.3 ( $\pm$ 30.1) for Hazelmere and 229.8 ( $\pm$ 56.4) for Inanda. The average TDS levels (mg/L) were: 90.4 ( $\pm$ 8.5) for Midmar, 128.5 ( $\pm$ 15.9) for Nagle, 208.5 ( $\pm$ 75.1) for Hazelmere and 251.2 ( $\pm$ 29.4) for Inanda. The average TOC levels (mg/L) were: 1.91 ( $\pm$ 0.35) for Hazelmere, 2.04 ( $\pm$ 0.39) for Midmar, 2.16 ( $\pm$ 0.26), for Nagle and 2.33 ( $\pm$ 0.27) for Inanda. The overall Redox potential values (mV) were (mean  $\pm$  SD) (median) (range): -14  $\pm$  (12) (-11) (range=-34 to 2) for all four dams. Individual values were: -18  $\pm$  (14) (-11) (-34 to -11) for Midmar, -13  $\pm$  (14) (-5) (-29 to -4) for Hazelmere, -11  $\pm$  (15) (-5) (-29 to 2) for Inanda, -9  $\pm$  (6) (-9) (-13 to -52) for Nagle. The average values for pH were (mean  $\pm$  SD): 6.77 ( $\pm$ 0.10) for Nagle, 6.79 ( $\pm$ 0.22) for Inanda, 6.86 ( $\pm$ 0.24) for Hazelmere and 6.94 ( $\pm$ 0.20) for Midmar.

Sample ID <sup>a</sup>	Water works/ Sample description/ Coagulant dose concentration	Month	Calibration method								
			M1 <sup>a</sup> Peak absorbance @ 690 nm		M2 Peak area @ 690 nm		M3 Ratio of peak absorbances ( $A_{690nm}/A_{520nm}$ )		"M1 and M2" combined data		
			Observed conc <sup>a</sup> (µg/L)	Observed% RSD	Observed conc (µg/L)	Observed% RSD	Observed conc (µg/L)	Observed% RSD	Calculated mean conc (µg/L)	Calculated SD (µg/L)	Calculated %RSD
4R	Wiggins: raw	May	3.16	7.09	4.21	4.83	38.2	1.03	3.69	0.74	20.15
5R	Wiggins: raw	May	4.23	10.8	3.73	15.1	nd <sup>a</sup>	0.92	3.98	0.35	8.88
Mean			3.70		3.97		38.20				
SD			0.76		0.34						
%RSD			20.48		8.55						
6F	Wiggins: potable	May	9.14	3.90	10.30	3.82	65.30	1.26	9.72	0.82	8.44
7F	Wiggins: potable	May	1.38	2.35	1.11	26.10	64.60	1.76	1.25	0.19	15.33
8F	Wiggins: potable	May	2.38	2.03	2.58	7.37	55.60	0.40	2.48	0.14	5.70
Mean			4.30		4.66		61.83				
SD			4.22		4.94		5.41				
%RSD			98.17		105.86		8.75				
9B	Wiggins: raw: Jar test	May	12.70	6.62	11.00	6.46	nd	3.01	11.85	1.20	10.14
10B	Wiggins: raw: Jar test	May	7.84	5.25	8.61	3.01	28.20	0.58	8.23	0.54	6.62
Mean			10.27		9.81		28.20				
SD			3.44		1.69						
%RSD			33.46		17.24						
11O	Wiggins raw: Jar test: optimal dose	May	22.70	7.86	21.30	7.34	nd	3.61	22.00	0.99	4.50
12O	Wiggins raw: Jar test: optimal dose	May	17.21						17.21		
13O	Wiggins/ optimal dose	May	14.10	3.01	19.10	1.50	nd	3.01	16.60	3.54	21.30
Mean			18.00		20.20			3.31			
SD			4.35		1.56			0.42			
%RSD			24.19		7.70			12.82			
14	Wiggins raw: Jar test; 30% overdose	May	1.90						1.90		
15	Wiggins raw: Jar test: 60% overdose	May	0.29	16.00	0.47	31.30	54.30	0.37	0.38	0.12	32.92
16	Wiggins raw: Jar test: 100% overdose	May	2.79	11.70	4.17	21.70	nd	2.39	3.48	0.98	28.04
20R	Wiggins: raw	June	3.60	4.34	4.11	9.75	48.20	0.98	3.86	0.36	9.35
20F	Wiggins: potable	June	0.713	3.39	1.53	2.04	15.3	0.38	1.12	0.58	51.51
21B	Wiggins: raw: Jar test	June	5.12	12.60	5.59	5.60	40.50	3.45	5.36	0.33	6.21
22B	Wiggins: raw: Jar test	June	1.49	4.90	1.95	5.20	22.70	0.17	1.72	0.33	18.91

Mean			3.31		3.77	5.40	31.60				
SD			2.57		2.57	0.28	12.59				
%RSD			77.66		68.27	5.24	39.83				
230	Wiggins: raw: Jar test: optimal	June	0.53	8.90	0.64	15.00	13.20	0.44	0.58	0.08	14.15
24	Wiggins: raw: Jar test: 30% overdose	June	3.64	8.10	4.41	2.72	42.80	1.01	4.03	0.54	13.53
25	Wiggins: raw: Jar test: 30% overdose	June	4.77	1.20	5.88	1.17	47.30	0.65	5.33	0.78	14.74
26	Wiggins: raw: Jar test: 30% overdose	June	1.78	5.09	2.16	8.85	30.90	5.46	1.97	0.27	13.64
Mean			3.40		4.15	4.25	40.33				
SD			1.51		1.87	4.06	8.47				
%RSD			44.45		45.15	95.63	21.01				
27	Wiggins: raw: Jar test: 60% overdose	June	5.65	0.48	7.35	0.07	35.60	0.50	6.50	1.20	18.49
28	Wiggins: raw: Jar test: 100% overdose	June	1.61	5.82	0.72	1.70	11.90	1.03	1.17	0.63	53.77
32R		July	3.93	7.19	4.00	7.57	47.20	0.97	3.97	0.05	1.25
32F		July	1.27	4.27	1.80	0.22	9.44	0.73	1.54	0.37	24.41
33B	Wiggins: raw: Jar test	July	5.51	0.63	7.21	1.79	54.20	0.80	6.36	1.20	18.90
34B	Wiggins: raw: Jar test	July	12.90	4.84	12.00	7.20	44.10	2.73	12.45	0.64	5.11
Mean			9.21		9.61		49.15				
SD			5.23		3.39		7.14				
%RSD			56.77		35.26		14.53				
350	Wiggins optimal	July	1.08	8.09	0.41	19.50	7.85	1.12	0.75	0.47	63.32
36	Wiggins 30% overdose	July	1.12	4.15	1.19	24.40	6.44	1.89	1.16	0.05	4.29
37	Wiggins 60% overdose	July	2.48	2.51	3.53	1.24	9.58	0.39	3.01	0.74	24.71
38	Wiggins 60% overdose	July	0.19	12.00	0.74	4.01	9.71	0.17	0.46	0.39	83.45
39	Wiggins 60% overdose	July	3.11	4.46	5.18	2.99	8.03	1.20	4.15	1.46	35.31
Mean			1.93		3.15		9.11				
SD			1.54		2.25		0.93				
%RSD			79.76		71.32		10.26				
40	Wiggins 100% overdose	July	2.70	2.52	2.16	6.52	10.20	1.26	2.43	0.38	15.71
1R	DV Harris: raw	May	6.79	7.15	6.61	7.72	nd	2.08	6.70	0.13	1.90
1F	DV Harris: potable	May	1.85	8.84	2.34	12.00	17.20	0.95	2.10	0.35	16.54
17R	DV Harris: raw	June	5.48	2.93	8.14	0.79	5.32	2.39	6.81	1.88	27.62
17F	DV Harris: potable	June	0.99	33.00	2.71	2.43	12.20	0.28	1.85	1.22	65.85
29R	DV Harris: raw	July	18.10	9.70	18.90	8.92	62.00	6.20	18.50	0.57	3.06
29F	DV Harris: potable	July	0.82	5.52	0.40	6.57	13.40	0.40	0.61	0.30	49.07
2R	Hazelmere: raw	May	1.43	2.06	2.30	0.41	23.30	0.33	1.87	0.62	32.99
2F	Hazelmere: potable	May	2.70	7.91	4.20	7.67	15.80	1.36	3.45	1.06	30.74
18R	Hazelmere: raw	June	17.25	0.95	23.80	0.69	52.20	0.83	20.53	4.63	22.57
18F	Hazelmere: potable	June	0.22	34.10	0.67	16.50	10.70	0.40	0.44	0.31	70.79
30R	Hazelmere: raw	July	1.78	4.33	2.31	0.65	16.80	0.69	2.05	0.37	18.33
30F	Hazelmere: potable	July	0.72	5.33	1.25	4.99	8.50	0.47	0.98	0.38	38.23
3R	Durban Heights: raw	May	13.30	4.70	13.40	6.36	nd	0.31	13.35	0.07	0.53
3F	Durban Heights: potable	May	2.01	23.80	2.87	15.10	57.00	2.12	2.44	0.61	24.92
19R	Durban Heights: potable	June	2.36	12.70	3.50	11.70	16.50	1.65	2.93	0.81	27.51
19F	Durban Heights: potable	June	0.89	8.68	0.95	9.66	13.80	0.40	0.92	0.04	4.61
31R	Durban Heights: raw	July	1.54	4.33	2.31	0.65	16.80	0.69	1.93	0.54	28.28
31F	Durban Heights: potable	July	8.02	1.54	11.20	0.99	26.00	0.29	9.61	2.25	23.40

\*conc.: Concentration; ID: Identity; nd: Not Detected.

**Table 2:** The observed levels of poly-DADMAC for all the samples.

Water works/dam	Coag. <sup>a</sup>	Dosing level: May-July (mg/L)	n	Poly-DADMAC concentration (µg/L)										Mean M3/M1	Mean M3/M2
				Calibration technique											
				Method 1 (M1)		Method 2 (M2)		Method 3 (M3)		Redox potential (mV)					
				Mean ± SD	%RSD	Mean ± SD	%RSD	Mean ± SD	%RSD	Mean ± SD	Median	Range			
Raw water															
Wiggins/Inanda			4	3.73 ± 0.46	12.30	4.01 ± 0.21	5.16	44.53 ± 5.51	12.37	-20 ± (18)	-27	-34 to +12	11.9	11.1	
DV Harris/Midmar			3	10.12 ± 6.94	68.54	11.22 ± 6.70	59.71	33.66 ± 40.08	119.07	-41 ± (49)	-41	-76 to -6	3.3	3.0	
Hazelmere/Hazelmere			3	6.82 ± 9.03	132.47	9.47 ± 12.41	131.05	30.77 ± 18.84	61.25	-32 ± (43)	-25	-79 to +7	4.5	3.2	
Durban Heights/Nagle			3	5.73 ± 6.57	114.52	6.40 ± 6.09	95.08	16.65 ± 0.21	1.27	-25 ± (1)	-25	-25 to -24	2.9	2.6	
Potable water															
Wiggins/Inanda	Z553D	0.08-1.01	4	3.40 ± 3.89	114.21	3.88 ± 4.32	111.45	50.20 ± 23.68	47.18	-11 ± (15)	-5	-29 to 1	14.8	12.9	
DV Harris/Midmar	Z553D	1.63-5	3	1.22 ± 0.55	45.19	1.82 ± 1.24	68.34	14.27 ± 2.61	18.30	-18 (14)	-11	-34 to -10	11.7	7.8	
Hazelmere/Hazelmere	SF3456	2-5	3	1.21 ± 1.31	108.06	2.04 ± 1.89	92.89	11.67 ± 3.74	32.10	-13 ± (14)	-5	-29 to -4	9.6	5.7	
Durban Heights/Nagle	SF3435	2.4	3	3.64 ± 3.83	105.36	5.01 ± 5.45	108.89	32.27 ± 22.27	69.02	-9 ± (6)	-9	-13 to -5	8.9	6.4	

**Table 3:** The computed mean residual poly-DADMAC values for the raw dam waters and corresponding potable water samples.

### Poly-DADMAC levels on raw and potable water

The observed levels of poly-DADMAC for all water samples is listed in Table 2; computed averages for the four raw dam water and associated potable waters are listed in Table 3 (Supplementary Figure A). The observed, residual poly-DADMAC levels, obtained by Method 1, (range: 6-16 µg/L) were, on average (±SD) (µg/L), for the raw water samples: 3.73 (±0.46) for Inanda Dam, 5.73 (±6.57) for Nagle Dam, 6.82 (±9.03) for Hazelmere Dam, and 10.12 (±6.94) for Midmar Dam (Table 3). The corresponding potable water levels (range: <2-8 µg/L), were: on average (±SD) (µg/L), 1.21 (±1.31) for Hazelmere Dam, 1.22 (±0.55) for Midmar Dam, 3.40 (±3.89) for Inanda Dam, and 3.64 (±3.83) for Nagle Dam. The observed, residual poly-DADMAC levels, obtained by Method 2, (range: 0-22 µg/L) were, on average (±SD) (µg/L), for the raw water samples: 4.01 (±0.21) for Inanda Dam, 6.40 (±6.09) for Nagle Dam, 9.47 (±12.41) for Hazelmere Dam, and 11.22 (±6.70) for Midmar Dam. The corresponding potable water levels (range: <2-11 µg/L), were: on average (±SD) (µg/L), 1.82 (±1.24) for Midmar Dam, 2.04 (±1.89) for Hazelmere Dam, 3.88 (±4.32) for Inanda Dam, and 5.01 (±5.45) for Nagle Dam. The observed, residual poly-DADMAC levels, obtained by Method 3, (range: 16.65-44.53 µg/L) were, on average (±SD) (µg/L), for the raw water samples: 16.65 ± 0.21 for Nagle dam, 30.77 ± 18.84 for Hazelmere Dam, 33.66 ± 40.08 for Midmar Dam and 44.53 ± 5.51 for Inanda Dam. The corresponding potable water levels, (range: 16.65-44.53 µg/L) were, on average (±SD) (µg/L), for the raw water samples: 11.67 ± 3.74 for Hazelmere Dam, 14.27 ± 2.61 for Midmar Dam, 32.27 ± 22.27 for Nagle dam, and 50.20 ± 23.68 for Inanda Dam.

## Discussion

### Physicochemical water quality

**Raw dam water:** For the 3-month study period, the average raw water turbidity increases in the order: Inanda (1.04) <Nagle<Hazelmere<Midmar Dam (9.38). For the raw water turbidity, the data indicates the lowest average value of 1 NTU for Inanda Dam, which is very much lower than that of the other three raw dam waters (5 for Nagle and 9 NTU for Midmar dam). The national drinking water

guide limit, as per the South African National Standards (SANS) 241: 2011, for turbidity is 1 NTU, and the Umgeni Water internal limit for potable water is lower, at ≤0.5 NTU. In general, very turbid waters will be expected to require a higher concentration of coagulant for flocculation during the water treatment process. This requirement is confirmed in the increasing dosage of poly-DADMAC that was used at the respective raw water treatment plants: the lowest dose being 0.08-1.01 mg/L, for Inanda Dam (1 NTU), up to a maximum 1.63-5 mg/L, for Midmar Dam (9 NTU). There is minimal difference in pH, which ranges from 6.8 for Inanda, to 7.2 for Midmar. These values do comply with the national SANS 241 limit of ≥5 to ≤9.7. The average conductivity and TDS levels increase in the order: Midmar <Nagle< Hazelmere< Inanda. Except for Inanda, all other three dam levels comply with the national SANS 241: 2011 potable water limit of ≤170 mS/m for conductivity, and ≤1200 mg/L for TDS. It is also evident that the coagulant blends, containing poly-DADMAC, function effectively as organic, polymeric flocculants, in lowering the raw water turbidity, from 5-9 NTU to the national limit of ≤1, for all four raw dam waters. The average TOC levels increase in the order: Nagle<Hazelmere<Inanda<Midmar. However, levels for all four dams comply with the national potable water guide (SANS 241: 2011) limit of ≤10 mg/L.

**Potable water:** The potable water turbidity values (NTU), much lower than the raw waters, indicate fairly good similarity for the three dams: Midmar (0.22), Nagle (0.25), and Inanda Dam (0.26), whilst that for Hazelmere is approximately three times higher (0.66 NTU). However, all values do comply with the national SANS 241: 2011 potable water quality limit of being ≤1 NTU. The average conductivity and TDS levels increase in the order: Midmar <Nagle<Hazelmere<Inanda. Except for Inanda (230 mS/m), all other three dam levels comply with the national SANS 241 potable water limit of ≤170 mS/m for conductivity, and ≤1 200 mg/L for TDS. For all four dams, the conductivity and TDS levels on the treated (potable) water exceed that for the corresponding raw dam water. Whilst there is no significant difference in TOC levels for all four dams, there is a noticeable lower TOC content in all the potable waters compared to the corresponding raw dam water.

### Method validation for the poly-DADMAC assay method

Detailed data has been previously reported [21]. The linearity range was between 0 and 30 µg/L with  $r^2=0.99$  in all cases. The method LOD and LOQ (µg/L) was 0.49 and 1.47 for Method 1 (absorbance of peak at 690 nm), 0.31 and 0.94 for Method 2 (area of peak at 690 nm) and 0.54 and 1.64 for Method 3 (ratio of the absorbance of peaks at 690 and 520 nm ( $A_{690nm}/A_{520nm}$ )). From the raw data supplied (Supplementary Material Text B), the computed instrument precision (% RSD) ( $\pm$ SD), based on signal response, was: 18.05 ( $\pm$ 17.65) for Method 1, 18.81 ( $\pm$ 18.44) for Method 2, and 3.24 ( $\pm$ 3.23) for Method 3. The overall mean within-batch (repeatability) precision (%RSD) for the triplicate assay values were: 7.42 ( $\pm$ 7.07) for Method 1, 7.66 ( $\pm$ 7.37) for Method 2, and 1.92 ( $\pm$ 2.71) for Method 3. The overall mean between-batch (reproducibility)%RSD was: 54.37 ( $\pm$ 30.03) for Method 1, 35.89 ( $\pm$ 34.89) for Method 2 and 13.50 ( $\pm$ 12.64) for Method 3.

### Observed residual levels of poly-DADMAC in all water samples

**Raw dam water samples:** Typical calibration graphs are shown in Figure 1 (Method 1: absorbance of peak at 690 nm), Figure 2 (Method 3: area of peak at 690 nm), and Figure 3 (Method 3: ratio of peak absorbances at 690 nm and 520 nm). The observed levels of poly-DADMAC for all the samples by all three calibration Methods 1, 2 and 3, are listed in Table 2 (Supplementary Figures C and D). After data processing, the observed mean values ( $\pm$ SD) (Table 3) were (µg/L), by Method 1, 2, and 3: 3.73 ( $\pm$ 0.46), 4.01 ( $\pm$ 0.21), 44.53 ( $\pm$ 5.51) for Wiggins WW, 10.12 ( $\pm$ 6.94), 11.22 ( $\pm$ 6.70), 33.66 ( $\pm$ 40.08) for DV Harris WW, 6.82 ( $\pm$ 9.03), 9.47 ( $\pm$ 12.41), 30.77 ( $\pm$ 18.84) for

Hazelmere WW, 5.73 ( $\pm$ 6.57), 6.40 ( $\pm$ 6.09), 16.65 ( $\pm$ 0.21) for Durban Heights WW. The typical UV-Vis spectra, for sample 4R (Wiggins WW: May), with the calibration standards, is shown in Figure 4. For assay values obtained by Methods 1 and 2, the poly-DADMAC levels, in the four dams, increase in the following order: Inanda < Nagle < Hazelmere < Midmar. However, for values obtained by Method 3, the order is: Nagle < Hazelmere < Midmar < Inanda.

**Potable (treated) water samples:** The observed levels of poly-DADMAC for all samples are listed in Table 2. After data analysis, the observed mean values ( $\pm$ SD) (Table 3) were (µg/L), by Method 1, 2, and 3: 3.40 ( $\pm$ 3.89), 3.88 ( $\pm$ 4.32), 50.20 ( $\pm$ 23.68) for Wiggins WW, 1.22 ( $\pm$ 0.55), 1.82 ( $\pm$ 1.24), 12.27 ( $\pm$ 6.21) for DV Harris WW, 1.21 ( $\pm$ 1.31), 2.04 ( $\pm$ 1.89), 11.67 ( $\pm$ 3.74) for Hazelmere WW, 3.64 ( $\pm$ 3.83), 5.01 ( $\pm$ 5.45), 32.27 ( $\pm$ 22.27) for Durban Heights WW (Table 3). The typical UV-Vis spectra, for sample 6F (Wiggin's potable: May), with the calibration standards, is shown in Figure 5.

For assay values obtained by Methods 1 and 2, the poly-DADMAC levels, for the four dams, increase in the following order: Midmar/ Hazelmere < Inanda < Nagle. However, for values obtained by Method 3, the order is: Hazelmere < Midmar < Nagle < Inanda.

### Determination of the UV-Vis spectra

The UV-Data were recorded once only; different mathematical models are applied to calculate the concentration. This one set of UV-data was then used in the 1 models (absorbance, area and ratio). The calibration was obtained using three techniques. The first approach involves plotting peak absorbance at 690 nm (corresponds to the

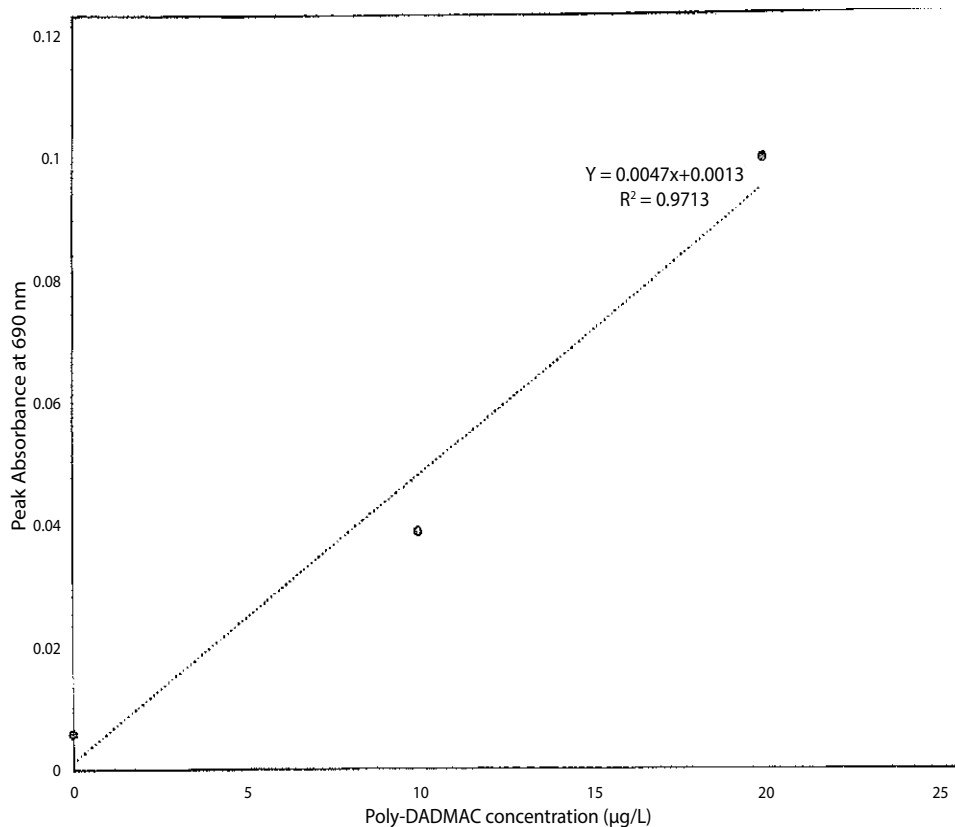


Figure 1: Calibration graph for raw dam water sample 4R by the peak absorbance Method 1.

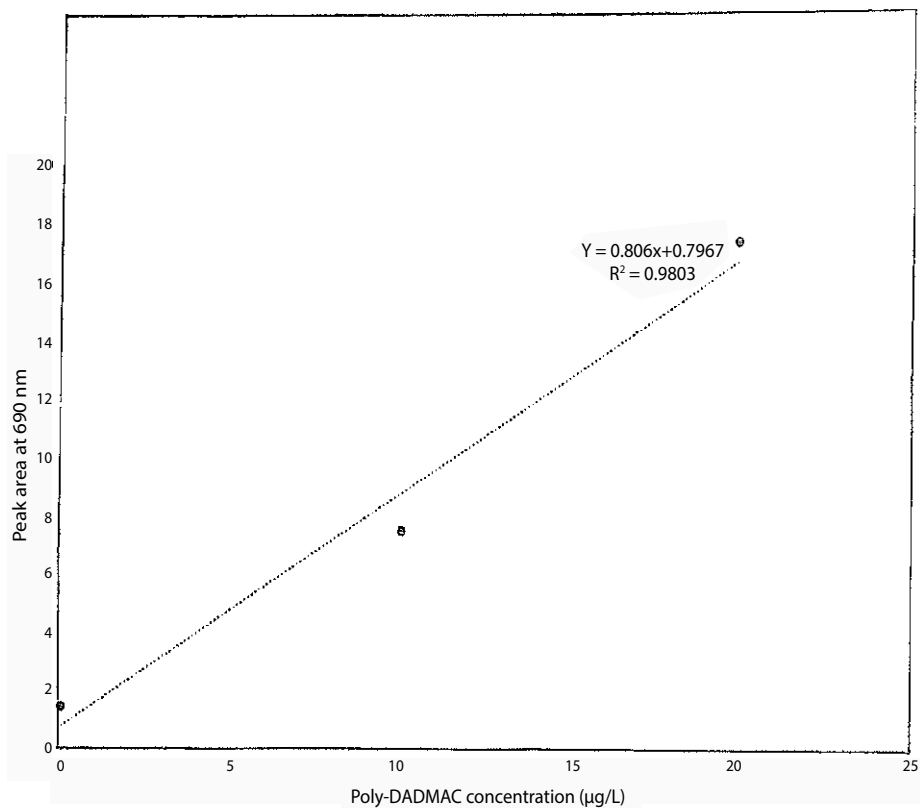


Figure 2: Calibration graph for raw dam water sample 4R by the peak area Method 2.

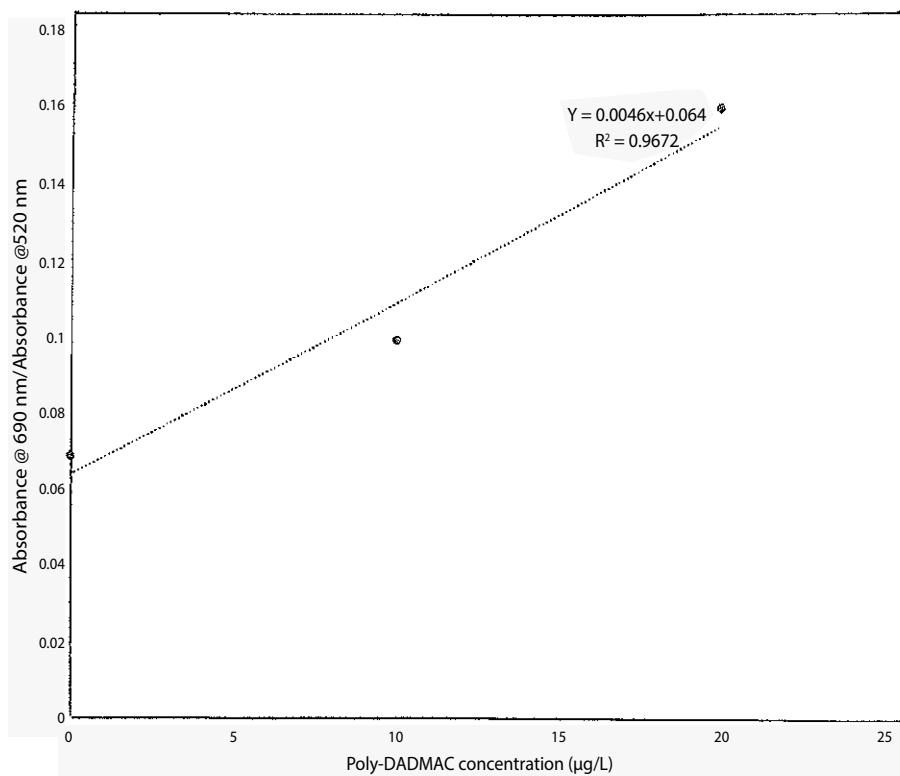


Figure 3: Calibration graph for raw dam water sample 4R by the ratio Method 3.



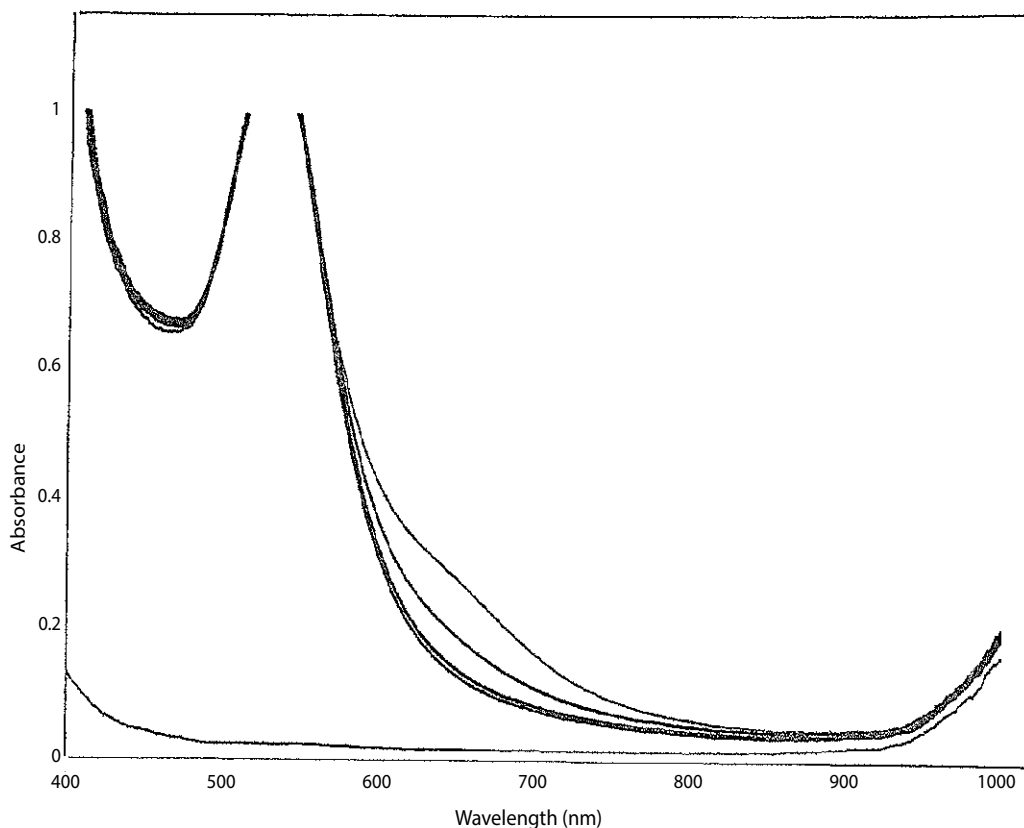


Figure 4: Typical UV-Vis spectra, for raw water sample 4R (Inanda Dam (Wiggins WW), May) with the calibration standards.

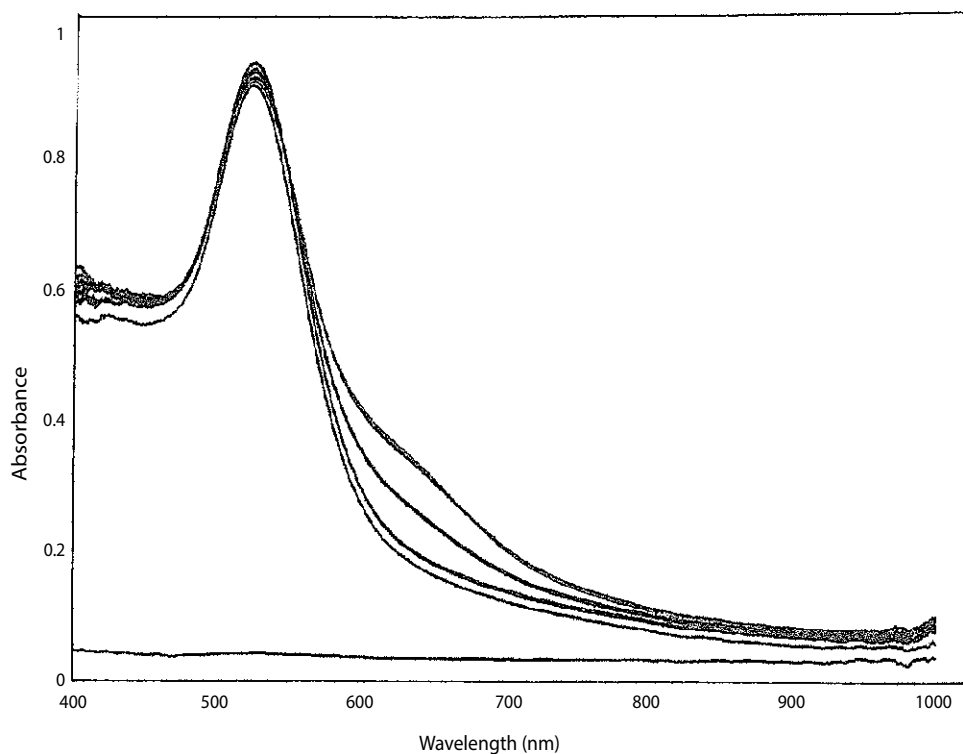


Figure 5: The typical UV-vis spectra, for potable water sample 6F (Inanda Dam (Wiggins), May), with the calibration standards.

aggregate of poly-DADMAC with gold nanoparticles) against poly-DADMAC concentration added to the sample, and then the poly-DADMAC concentration is calculated from the equation of the line where the  $y$ -intercept is equal to zero (Method 1). The second approach is similar, but instead the area of the peak at 690 nm is used (Method 2). The rationale for using the area is due to the fact that there is a distribution of poly-DADMAC-gold nanoparticle aggregates, and the area could account for the inherent variations with the aggregates [21]. The third method used a similar approach; however, the response parameter was the ratio of the peak absorbance at 690 nm and at 520 nm ( $A_{690nm}/A_{520nm}$ ) (Method 3). The ratio method is the preferred method in the literature [24], and as per the earlier work, this method of analysis was also done in order to determine which of the three methods of data analysis provides the most accurate and precise results with the "real world" water samples.

### Comparison of assay values for poly-DADMAC obtained by the 3 Methods

Inspection of the observed assay data for poly-DADMAC on all the water samples indicate, in general, fairly good comparison between the Method 1 and Method 2 values, while the values obtained by Method 3 are much higher (Supplementary Figure B). Considering the LOQ ( $\mu\text{g/L}$ ) for each of the Methods [21], (1.47 for Method 1, 0.94 for Method 2, 1.64 for Method 3) assay values for samples 7F, 17F, 18F, 19F, 20F, 29F, 30F, 32F, 2R, 15, 36, 38, 23O and 35O (fourteen in total) were below the LOQ (1.47  $\mu\text{g/L}$ ) for Method 1; assay values for samples 18F, 29F, 15, 28, 38, 23O and 35O (seven in total) were below the LOQ (0.94  $\mu\text{g/L}$ ) for Method 2, and assay values for samples 1R, 3R, 5R, 16, 11O, 13O (six in total) were below the LOQ (1.64  $\mu\text{g/L}$ ) for Method 3. For both Methods 1 and 3, there was agreement for assay values for six samples: 18F, 29F, 15, 38, 23O and 35O, which were below the respective LOQ of the methods. Simple correlation analysis by linear regression of the assay values by all 3 Methods indicated fairly good correlation for assay values obtained by Method 1 and Method 2:  $r^2=0.9415$  ( $y=1.059x+0.4607$ ) (Supplementary Figure A); the corresponding comparison for Method 1 and Method 3 values gave  $r^2=0.3021$  ( $y=2.4848x+18.394$ ), and the Method 2 and Method 3 comparison gave  $r^2=0.2504$  ( $y=1.917x+18.949$ ), indicating no significant correlation. For confirmation, the statistical data analysis indicated that, for the comparison of poly-DADMAC values obtained by all three Methods (1, 2 and 3), there was no significant difference for the poly-DADMAC levels for 31 samples, obtained by Methods 1 and 2 (Supplementary Table B).

### Performance evaluation of the analytical test method for poly-DADMAC

**Observed precision of poly-DADMAC concentrations:** Except for samples 14 and 12O, all samples ( $n=49$ ) were analyzed in triplicate by the three techniques. The instrument precision data indicates that the precision (%RSD  $\pm$  SD) for Methods 1 ( $18.81 \pm 18.44\%$ ) and Method 2 ( $18.05 \pm 17.65\%$ ) exceeds the  $\leq 10\%$  Relative Standard Deviation (RSD) limit used in our internal method validation laboratory procedure. Method 3 ( $3.24 \pm 3.23\%$ ) appears to be the most precise. Based on the 49%RSD values, the overall mean within-batch precision (% RSD) ( $\pm$ SD) for the triplicate assay values were: 7.42 ( $\pm 7.07$ ) for Method 1, 7.66 ( $\pm 7.37$ ) for Method 2, and 1.92 (2.71) for Method 3. All three methods thus have repeatability RSD  $\leq 10\%$ , and the data indicates that the ratio method (Method 3), with the lowest %RSD, is the most precise. For those 8 samples that were analysed for  $n=2-4$  times, over different days during the three months, the overall mean between-

batch reproducibility (%RSD) ( $\pm$ SD) was: 54.37 ( $\pm 30.03$ ) for Method 1, 35.89 ( $\pm 34.89$ ) for Method 2, and 13.50 ( $\pm 12.64$ ) for Method 3. Again, the ratio method (Method 3) is the most precise. Our internal laboratory procedure for method validation of analytical test methods, for water, wastewater, and soil/sludge matrix, is based on the criteria in the TR reference document (TR 25-02), published by the local ISO/IEC 17025 accrediting body South African National Accreditation Standards (SANAS), and is traceable to the ISO/IEC 17025 guide for method development and validation of test methods for testing and calibration laboratories. Our specified precision limit is RSD  $\leq 10\%$ . The observed reproducibility precision for Methods 1 and 2 is very much greater than 10% (54 and 36%), which exceeds the international limits, whilst that for Method 3 is just over 10% (13%), again indicating that the Ratio Method 3 is the most precise. However, it must be noted that the calculated reproducibility precision is based on data over this lengthy three-month (90 days - May to July) study period. In the initial report [21], intra and inter-day precision ranged from 0.1-0.7% RSD for all three methods. However, this precision was obtained on poly-DADMAC standards (30-90  $\mu\text{g/L}$ ) in laboratory water, and not on real environmental sample matrix. It is not clear as to the number of different days the reproducibility precision data was obtained. Furthermore, precision data at the lower, reported LOQ (2  $\mu\text{g/L}$ ) level for poly-DADMAC, for all three Methods, was not reported [21].

**Accuracy of the poly-DADMAC assay values:** The method validation data from the initial report [21] indicated recovery values (%error) of: 87-97% (-3 to -12%) for Method 1, 92-98% (-2 to -8%) for Method 2 and 92-89% (-8 to -11%) on poly-DADMAC solutions (30  $\mu\text{g/L}$ ), presumably in ultrapure water matrix, spiked at 10 and 20  $\mu\text{g/L}$ . However, no recovery data is reported for blank matrix, or real samples, spiked at less than 10  $\mu\text{g/L}$ , and/or at the LOQ level ( $\leq 2$   $\mu\text{g/L}$ ). The method was also validated for selectivity where solutions containing DADMAC monomer and choline chloride were spiked with poly-DADMAC [21]. One of the major, and significant, raw materials used in poly-DADMAC synthesis, is the DADMAC monomer. Although the actual percentages are not known, it is a known fact that the commercial blends of the organic coagulants do contain some minor level of the DADMAC monomer. Their relative, residual concentration in the potable water will depend on their removal by the water treatment process at each water treatment works, which in turn is influenced by various factors. Polyelectrolyte applications in potable water production and industrial waste water treatment are in the coagulation and flocculation steps, and dewatering of treatment plant sludge. Polyelectrolytes have strong tendency to adsorb onto surface of particles in aqueous suspension, and is the main reason they are widely used in water treatment processes. The water industries are responsible for producing safe drinking water for people and all organisms in rivers, lakes and oceans. To keep water safe, polyelectrolytes are required to mix with turbid natural water for removing solid waste material before filtration. The main aim of introducing polyelectrolytes in water treatment is to induce flocculation and coagulation processes for the removal of suspended solid particles (colloidal matter). All waters, especially surface water, contain both dissolved and suspended particles, which are often assumed to be negatively charged. In suspension, particles repel each other and they cannot come together (stay stable in solution). As a result, they will remain in suspension. Coagulation is the processes where polyelectrolytes are added to destabilize the suspension or affect the surface of water. In coagulation, polyelectrolytes, overcome the factors that keep particles apart such as repulsion forces, and enable the particles to come together to form micro-flocs (flocs are cluster of small particles). In the flocculation

process, polyelectrolytes are further added to induce the agglomeration of micro-flocs to form macroflocs (bigger particles). The macro-flocs, containing poly-DADMAC, settle or precipitate out of water and are removed as sludge. In our study, the observed values indicate significant poly-DADMAC levels (range: 2-24 µg/L) for all the raw dam water samples, by all three Methods. These levels are approximately two times higher compared to the corresponding levels in the treated water (range: 2-11 µg/L). Raw dam water, treated with poly-DADMAC-containing coagulant will be expected to contain some residual polymer present in the potable water, not removed by the sand filtration, or in the final sludge, estimated at ≤50 µg/L. The observation of the lower levels in the potable water indicates efficiency of the raw water treatment process in removing the added poly-DADMAC coagulant. The observed levels of residual poly-DADMAC on the 4 potable waters in this study indicate compliance to the international limit of ≤50 µg/L and accuracy of this gold nanoparticle test method. Raw dam water, in the absence of environmental contribution, will not be expected to contain any, or significant levels, of poly-DADMAC. However, the much higher levels noted on our raw water suggests a possible inaccuracy of this gold nanoparticle test method. Alternatively, some other organic compound/s, that are present in the raw dam water, forms an aggregate with the citrate-capped Au-NPs and is subsequently detected by the colorimetric method.

**Redox potential:** The potential at the boundary (surface of hydrodynamic shear) is the zeta potential. The magnitude of the zeta potential gives an indication of the potential stability of the colloid system. In this study, the zeta potential of the water samples was not determined. The redox potential (or reduction potential) is the tendency of a chemical species to acquire electrons and thereby be reduced. In short, a numerically positive redox potential represents an environment conducive to the oxidation of an introduced substance by reduction of the original media. The redox potential showed a trend of being relatively negative for the raw waters (higher levels of poly-DADMAC) and relatively positive for the potable waters (lower levels of poly-DADMAC) (Supplementary Figures E and F). A decrease in zeta potential, towards negative values, was noted for the citrate-capped Au-NPs (and the other capped Au-NPs) when titrated with TOC as humic acid [25].

### **Possible sources for the observed levels of apparent poly-DADMAC in the raw water**

**Environmental contribution of poly-DADMAC:** If the observed levels on the raw dam waters is really due to presence of poly-DADMAC, the corresponding catchment and its associated environmental factors, needs to be considered as a potential source: e.g., residence time, closeness of industries, sewage infiltration, agricultural activity, use of poly-DADMAC, the natural, mechanical mechanism of poly-DADMAC-floc aggregate removal by settling to the bottom of the dam by gravity, etc. The four dams supply raw water to the corresponding water treatment plants. The associated environmental data for each dam is summarised in Supplementary Table C. While the process effluent is returned to the Head of Works at Durban Heights (Nagle Dam) (Supplementary Table C), the average poly-(DADMAC) (3.64 µg/L) is not very different from that observed for Wiggins WW (Inanda Dam) (3.40 µg/L) (Table 3). Overall, the data indicates fairly negligible possibility of the environment as a source of poly-DADMAC.

**Application of gold nanoparticles:** Nanoparticles are one of the most important nanomaterials and they are defined as any material with at least one dimension in the 1-100 nm range. The particle shape may vary and the materials include metals, semiconductors,

polymers and carbon based materials. Gold nanoparticles have unique and very interesting physical-chemical properties, especially their optical properties. Like all other metal nanoparticles, Au-NPs undergo plasmon resonance, whereby the frequency of the incident electromagnetic radiation resonates with the oscillation of the delocalised electron cloud present on the nanoparticle surface. The localised surface plasmon resonance frequency lies in the visible range for Au-NPs, and because it is very sensitive to: diameter of the Au-NPs, the surrounding surface chemistry, the aggregation of Au-NPs, it has found use as a probe, or sensor, for the detection of large and small biomolecules, various organic molecules and some inorganic ions [25-30].

**Characterisation of the Au-NP complex:** When gold nanoparticles are introduced into the poly-DADMAC solution, the intense red colour, (which shows an absorbance peak at 526 nm), of the Au-NPs decrease, with a slow appearance of a blue colour. The colour change is due to the shift of the plasmon band to longer wavelengths as the Au-NPs aggregate. The blue colour is attributed to the formation of aggregates between the Au-NPs and poly-DADMAC. Two possible scenarios have been proposed [21] poly-DADMAC has replaced the citrate ions on the surface of the Au-NPs, or, the poly-DADMAC has simply surrounded the citrate ions that are absorbed onto the Au-NPs. The Au-NPs have a high affinity for nitrogen and cationic molecules compared to citrate ions [25-29]. Thus, the former scenario is more likely, where the poly-DADMAC replaces the citrate ion, and destabilises the colloid with aggregate formation. In the current study, the aggregates of Au-NPs and poly-DADMAC are characterised by UV-Vis spectroscopy and TEM. In Figure 5, the peak at 526 nm is due to excess Au-NPs and a second peak at 690 nm, is due to the Au-NP-poly-DADMAC aggregates. The observation of the 164 nm shift to longer wavelengths is due to the formation of Au-NP-poly-DADMAC aggregates, which was confirmed by TEM analysis [21]. Other changes that can occur with NPs, beside aggregation that can cause a shift in the plasmon peak are: refractive index of the surrounding medium, surface chemistry of the Au-NPs, and changes with Au-NP size or shape [27,29,31]. The particle size analysis of the aggregates revealed that the Au-NPs have a similar morphology, before aggregation ( $27 \pm 3$  nm) and after aggregation ( $28 \pm 3$  nm) [21]. The Au-NP optical properties change with the size. Based on size alone, a shift of colour from red to blue occurs when the particle size changes from 3 to 60 nm [27,29]. Thus the shift in the plasmon resonance peak cannot be due to a change in size or shape of the Au-NPs, but it is due to the aggregation of the Au-NPs with poly-DADMAC [21].

**Natural organic matter (NOM):** NOM is a mixture of organic compounds, having diverse chemical properties, which occur in all natural water sources as a result of the breakdown of animal and plant material [32]. Since NOM emanates from different sources, it can be assumed that the composition of NOM in various water sources may not be uniform. NOM can be broadly characterised into: humic substances, microbial by-products and colloid natural organic matter. Humic substances constitute the more hydrophobic fraction of NOM and exhibit relatively high specific ultraviolet absorbance (SUVA) values since the humics usually contain a relatively large proportion of aromatic moieties. Huber et al. reported the characterisation of aquatic (river sample in Germany) humic and non-humic matter using size exclusion chromatography (SEC) [33] into biopolymers, humic substances, building blocks, low molecular weight acids, low molecular weight neutrals and hydrophobic organic carbon. The typical organic content (NOM) of raw dam water is biopolymers, which are very high in summer, and moderate in winter (250-800 µg/L), and humics (moderate: ±2,000 µg/L) [Huber S, Personal Communication, 2015].

Natural organic matter in eight South African water treatment plants, including Wiggins Water Works, of Umgeni Water, was characterized using combined techniques [34,35]. The dissolved organic carbon (DOC) results varied from 3.5-22.6 mg/L, indicating the extent of variation of NOM quantities in the different regions where the samples were obtained. The advanced techniques used indicated that the samples contained mainly humic substances, while some had marine humic and non-humic substances.

**Reactions of NOM with Au-NPs:** Nason et al. [35] studied the interactions between NOM and gold nanoparticles, stabilized with different organic capping agents, like anionic citrate, neutral polyvinylpyrrolidone, and cationic mercapto (trimethylammonium). Another report appeared on the gold(III) and Au-NPs interactions with humic acids [35,36]. A study on effects of NOM type and concentration on the aggregation of citrate-stabilized Au-NPs was further reported by Nason et al. [37]. They showed that four different NOM isolates act to stabilize citrate Au-NPs with respect to aggregation. The resulting stability appears to be due to adsorption of the NOM onto the surfaces of the NPs; the exact nature of the interactions between NOM and the coated Au-NPs is however, unclear. Both the type and concentration of NOM, along with the ionic strength of the system are important factors in determining the colloid stability.

**Possible explanation for apparent poly-DADMAC levels in the Umgeni Water catchment (raw dam waters):** NOM can be broadly characterized into: humic substances (HS), microbial by-products (composed of acids, with high charge density, polysaccharides, amino sugars, proteins), and colloidal natural organic matter (contain relatively polar amino sugars). Treatment of raw dam water, containing, inter alia, NOM, and other matter, with coagulant, like poly-DADMAC, removes NOM, and other matter, by floc formation, and subsequent filtration. Untreated raw dam water, not treated with coagulant, will contain the same concentration of NOM, and other matter.

The Au-NP colorimetric method, in this study, uses 20 mL of a suspension of about 200 particles per 410 mL, equivalent to  $\pm 10$  particles per sample/test. Examination of the typical UV-Vis spectrum of the gold nanoparticle solutions mixed with various concentrations of poly-DADMAC standards (10-100  $\mu\text{g/L}$ ) [21] shows the presence of the peak for the Au-NPs, at 520 nm, and the Au-NP-poly-DADMAC aggregate (690 nm), suggesting an excess amount of Au-NPs is still available for possible aggregate formation with other organic compounds, even at 100  $\mu\text{g/L}$  poly-DADMAC concentration. Based on the earlier studies [35-37], we therefore propose that, on addition of Au-NPs to the raw water sample, there is some interaction of the NOM and Au-NPs to form aggregates, which are subsequently detected as "poly-DADMAC", by the colorimetric analytical method employed for determination of residual poly-DADMAC. Presumably, the Au-NP-(NOM) aggregate absorbs at the same wavelength of 690 nm, as the Au-NP-(poly-DADMAC) aggregate.

**Influence of sample collection from different sites at different times:** This is an important factor that must be considered in the evaluation of the analytical results obtained, and the subsequent conclusions made in this study. The grab, raw and potable, water samples in this study were collected over a 3-month period, from the designated sample sites, but on different days, and at different times. The day-today variation (%RSD) for water quality indices, and for residual poly-DADMAC levels, can therefore be expected to be fairly large. For example, for raw water, the %RSD for TOC ranges from 5-19%, and is 12-19% for potable water. For raw water, the %RSD for the apparent poly-DADMAC levels, by Method 1, ranges from

12-132%, and is fairly similar for potable water: 45-114%. The much higher variation in poly-DADMAC levels, in both raw and potable water, compared to variation for both a raw and potable, water quality index, can be due in part to, amongst others, the following factors: the much smaller number of samples ( $n=3-4$ , for poly-DADMAC, Table 3), compared to  $n=90$  (for TOC, Table 1), and the relatively higher inherent imprecision noted for Method 1 (absorbance of peak at 690 nm) and Method 2 (area of peak at 60 nm), variation in the NOM levels in the various water samples taken.

**Earlier work on poly-DADMAC quantitation in river water:** Gumbi et al. [21] reported relatively lower levels of poly-DADMAC (not detected/2-2.1  $\mu\text{g/L}$ ) on samples ( $n=8$ ) from the Umgeni River, in KwaZulu-Natal, using the same citrate-capped, gold nanoparticle colorimetric method. Again, one would not expect any, or significant, levels of poly-DADMAC, in natural river water. The corresponding TDS levels for these river samples were correspondingly lower: (mean ( $\pm$ SD)) 41 ( $\pm$ 25) mg/L (range=18-69); the TOC levels on these river samples were not, however, reported [21]. For our raw dam waters, we observed an average TOC level of 2.6 ( $\pm$ 0.40) mg/L for the raw waters. The apparent mean poly-DADMAC levels measured were 6.6  $\mu\text{g/L}$  (range= $<2$  to 17  $\mu\text{g/L}$ ), with much higher TDS levels of 144 ( $\pm$ 68) mg/L (range=65-244). Based on our findings in this study, the possibility exists similarly that the apparent levels of 2  $\mu\text{g/L}$  noted in the earlier report [21] could be likely due to a relatively lower level of NOM (not reported) in river water, which forms an aggregate with the citrate-capped Au-NPs, and is detected by the UV-Vis colorimetric method.

**Removal of NOM from water:** Krause, et al. [32], in their characterisation of NOM in South Africa, investigated the use of cyclodextrin polyurethanes for NOM removal; the hydrophobic basic fraction and the hydrophilic acid fraction were most efficiently removed (24 and 10% respectively). The use of strong base anion exchange resin in the sample, about 10 g/50 mL, and shaking overnight [Huber S, 2015, Personal Communication] may remove most of the NOM while poly-DADMAC should stay in solution; the resin is cationic in charge and should repulse poly-DADMAC.

### Evaluation of the application of the developed Au-NP colorimetric method

Although citrate-Au-NPs were synthesised in the present study, they are commercially available from NanoComposix Inc. and nationally (South Africa) ( $1.67 \times 10^{11}$ - $1.97 \times 10^{11}$  particles/mL), but at substantial cost:  $\pm$ R266 per 20 mL/sample. Beside this reagent cost, there are no other major reagent costs. The capital costs of the required equipment are affordable ( $\pm$ 7394 Euros). Regarding the method performance, detailed data has been previously reported [22]. The linearity range was between 0 and 30  $\mu\text{g/L}$  with  $r^2=0.99$  in all cases. The method LOD and LOQ ( $\mu\text{g/L}$ ) was 0.49 and 1.47 for Method 1 (absorbance of peak at 690 nm), 0.31 and 0.94 for Method 2 (area of peak at 690 nm) and 0.54 and 1.64 for Method 3 (ratio of the absorbance of peaks at 690 and 520 nm ( $A_{690\text{nm}}/A_{520\text{nm}}$ )), indicating that Method 2 is the most sensitive. However, all three Methods are fairly sensitive, for the quantification of residual poly-DADMAC as the international maximum limit is about 25 times higher. However, the recovery (and percentage error) at this level was not reported [22]. The Method detection level (MDL) has been defined as follows: "the constituent concentration that, when processed through the complete method, produces a signal with a 99% probability that it is different from the blank. For seven replicates of the sample, the mean must be 3.14s above the blank where s is the standard deviation of the seven replicates...The MDL will be larger than the LLD...Recoveries should

be between 50 and 150% and %RSD values  $\leq 20\%$ ...” [38,39]. The Level of quantitation (LOQ) (Minimum quantitation level (MQL)) has also been defined as follows: “the constituent concentration that produces a signal sufficiently greater than the blank that it can be detected within specified levels...Typically it is the concentration that produces a signal 10s above the reagent water blank signal” [38].

The IUPAC method [39] uses the mean concentration and standard deviation from replicate analysis of a “blank” (ultrapure water) sample matrix, as per following equations: mean+10 SD, for LOQ, and mean+3 SD, for Limit of Detection (LOD), respectively. This statistical approach, however, cannot be applied when a negative value is observed for the signal response for the blank sample. The serial dilution technique, although it results in higher LOD and LOQ, would tend to be more accurate, being based on compliance to actual recovery, and precision, limits; selection of the “noise” region in a chromatogram, using the S/N method, is subjective, due to choice by the analyst. The computed instrument precision (% RSD) ( $\pm$ SD) was 18.05 ( $\pm$ 17.65). The overall mean within-batch precision (% RSD) for the triplicate assay values were: 7.42 ( $\pm$ 7.07) for Method 1, 7.66 ( $\pm$ 7.37) for Method 2, and 1.92 (2.71) for Method 3, which complies with our internal limit of  $\leq 10\%$  RSD for method validation. The overall mean between-batch reproducibility was, however  $\geq 10\%$  RSD for all three calibration methods: % RSD ( $\pm$ SD): 54.37 ( $\pm$ 30.03) for Method 1, 35.89 ( $\pm$ 34.89) for Method 2, and 13.50 ( $\pm$ 12.64) for Method 3. Method 3 was the most precise, and most inaccurate. Compared to other analytical methods, like colloid titration and gravimetry, this gold nanoparticle method is much faster, is far less labour-intensive and is much more sensitive.

### Correlation analysis between observed residual poly-DADMAC levels and water quality parameters

The average poly-DADMAC levels, obtained by all three calibration methods (M1, M2, M3) on all raw and potable water, were compared with the corresponding average pH, conductivity, turbidity, TDS and TOC values. The results of all the statistical data analysis is summarised in Supplementary Table D. Due to the fairly good correlation of poly-DADMAC levels obtained by M1 and M2, any comparisons, and their possible significance, between poly-DADMAC levels obtained by M3 and water quality parameters can be ignored.

**Raw water:** For raw water, there was a strong positive linear relationship between: the apparent poly-DADMAC (M1) level and TOC, poly-DADMAC (M1, M2) level and pH, and poly-DADMAC (M1, M2) level and turbidity. A strong negative relationship between: the apparent poly-DADMAC (M1, M2) level and Conductivity, poly-DADMAC (M1, M2) level and TDS, poly-DADMAC (M1, M2) level and Redox Potential was observed.

It was subsequently proposed that the observed, apparent poly-DADMAC levels are due to the presence and reaction of NOM with the Au-NPs. In such a case, it can be expected that water quality parameters, like TOC, TDS, conductivity (NOM contains some charged material) and turbidity of water would increase as the apparent poly-DADMAC (NOM, indicated by the TOC level) levels increase. However, a strong negative relationship is noted for the comparison with conductivity and TDS. In the absence of actual NOM levels, there will be obvious uncertainty in these comparisons. Particles that occur in natural waters are almost always negatively charged. Thus, as apparent poly-DADMAC (NOM) levels increase, redox potential will decrease (shift toward negative values). The raw water pH for the four dams ranged from 6.8-7.1. Acidic pH is known to destabilise citrate-

capped Au-NPs [30]. Gumbi et al. [22] showed that varying the pH (6-9) did not have any significant effect on absorbance or area for this colorimetric method for poly-DADMAC analysis. It would appear that NOM behaves similarly to poly-DADMAC, so that an increase in apparent poly-DADMAC level is noted with increasing pH.

**Potable water:** For potable water, there was a strong positive linear relationship between: the poly-DADMAC (M1, M3) level and TOC, poly-DADMAC (M1, M2) (level) and Redox potential. A strong negative relationship between the poly-DADMAC (M1, M2, and M3) level and pH was noted. The TOC levels can be expected to increase with an increase in poly-DADMAC (organic material) levels. Poly-DADMAC is a cationic (positively charged) polymer. Hence, an increase in level would be expected to result in increasing (positive) Redox potential. The potable water pH for the four treated dam waters ranged from 6.8-6.9, which is not very different to that of the corresponding raw waters, and it falls within the reported stable range studied [21]. Although the sample numbers in this study is rather small ( $n=4$ ), it would appear that optimum levels of poly-DADMAC (3.4-3.6 mg/L) are observed at average water pH 6.77 (Nagle Dam) and 6.79 (Inanda Dam).

**Possible relationship between NOM and poly-DADMAC:** Grab raw and potable water samples in this study were collected over a 3-month period, from the designated sample sites, but on different days, and at different times. The day-to-day variation (%RSD) for water quality indices, and for poly-DADMAC levels, can therefore be expected to be fairly large. For example, for raw water, the %RSD for TOC ranges from 5-19%, and is 12-19% for potable water. For raw water, the %RSD for the apparent poly-DADMAC levels, by Method 1, ranges from 12-132%, and is fairly similar for potable water: 45-114%. The much higher variation in poly-DADMAC levels, in both raw and potable water, compared to variation for both a raw and potable, water quality index, can be due in part to, amongst others, the following factors: the much smaller number of samples ( $n=3-4$ , for poly-DADMAC, Table 3), compared to  $n=90$  (for TOC, Table 1), and the relatively higher inherent imprecision noted for Method 1 (absorbance of peak at 690 nm) and Method 2 (area of peak at 60 nm), variation in the NOM levels in the various water samples taken. The TOC value is approximately equal to the NOM value for natural waters. Humic acid, a component of NOM, has been suggested as a standard for mimicking NOM in the laboratory. In the performance of Total Organic Carbon (TOC) analysis, UV persulfate instrumentation demonstrated 95% recovery of humic acid consistently across a linear range of 1 to 100 ppm C, the range typically found in the NOM of source water. In this study, there is a strong positive linear relationship between the poly-DADMAC level (determined by M1) and TOC, for both raw and potable water. The NOM levels were not determined analytically in this study. We can therefore expect some positive linear relationship between the NOM (not measured here) and poly-DADMAC levels. The observed/measured TOC levels can be used as an approximate indicator of the actual NOM levels. Raw dam water, not treated with coagulant, will contain NOM and other material, whereas potable water, treated with coagulant, will contain a much lower level of NOM and other material, due to the effect of the coagulant during the water treatment process. Subsequently, the apparent poly-DADMAC levels, from reaction of NOM with the Au-NPs, would be expected to be greater for the raw water, compared to the potable water. The TOC levels are, in general, expected to be greater for raw water (contains NOM, various organic matter, etc.) compared to treated, potable water (added coagulant aids in NOM, organic matter, etc. removal via flocculation-coagulation during the water treatment process). This is evident for each of the four

dams. The TOC levels are as follows (raw vs. potable – mg/L): Inanda: 2.59 vs. 2.33; Nagle: 2.31 vs. 2.16; Hazelmere: 2.48 vs. 1.91; Wiggins: 3.17 vs. 2.04. We would therefore expect the NOM levels for the raw dam waters to exceed that for the treated potable water. Subsequently, the apparent (false positive) poly-DADMAC levels noted for raw water, from the proposed reaction of NOM in raw water, with the Au-NPs, would be expected to be greater than the actual true level of residual poly-DADMAC in the treated potable water (which contains a relatively lower level of NOM, organic matter, etc.). The source of residual poly-DADMAC in the treated water is from the initially added coagulant (0.08-5 mg/L) during the water treatment process, and is expected to be  $\leq 50 \mu\text{g/L}$ , the international limit. The latter is observed in this study. The observed poly-DADMAC levels are as follows (raw vs. potable –  $\mu\text{g/L}$  (Method 1): Midmar: 10.12 vs. 1.22; Hazelmere: 6.82 vs. 1.21; Nagle: 5.73 vs. 3.64; Inanda: 3.73 vs. 3.40. Compared to the other 3 dams, the average raw water turbidity for Inanda dam is distinctly the lowest ( $1.04 \pm 0.30$  NTU), and so is the corresponding coagulant dosing level (0.08-1.01 mg/L) (Table 3) required. Hence there is no significant difference in the apparent poly-DADMAC level in the raw water (3.73), and the treated water (3.40). A combined plot of TOC (converted to  $\mu\text{g/L}$  units) (x-axis) vs. poly-DADMAC concentration (y-axis) indicated a significant positive linear relationship:  $r^2=0.8017$ . We can therefore expect a significant positive linear relationship between the actual NOM and poly-DADMAC levels.

### Degradation of poly-DADMAC

Detailed stability studies on poly-DADMAC were conducted by John [19], under different experimental conditions of exposure to temperature (ambient to  $80^\circ\text{C}/30$  min), pH variations (2-12/1 hr.), UV radiation (365 nm/24 hr.) and ozone. At  $80^\circ\text{C}$  there was clear change in polymer structure. At pH 12, there was a noted decrease in the polymer peak area, but peak shape and MWD remained essentially unchanged. The UV radiation study showed evidence of polymer degradation. In essence, the GPC results indicated that poly-DADMAC is a very stable polymer and undergoes change only when subjected to extremes of pH, temperature and UV conditions, which are unlikely to be experienced under environmental conditions, and during the normal course of water treatment processes. The stability data on poly-DADMAC indicate very little or no effect on the validity or accuracy of our observed study results.

### Conclusion

The current real world study indicates that the citrate-capped gold nanoparticle colorimetric method, using the calibration of peak absorbance at 690 nm (Method 1), or peak area at 690 nm (Method 2), is suitable for quantification of residual poly-DADMAC in potable water, treated with the poly-DADMAC coagulant. However, raw dam water, containing NOM, and possibly any other organic matter that may be present, apparently forms an aggregate with the citrate-capped Au-NPs, which absorbs at the same 690 nm wavelength as that of the Au-NP-poly-DADMAC aggregate and is subsequently detected by the UV-Vis colorimetric method. The test method was found to be sensitive (LOQ= $0.9\text{-}1.6 \mu\text{g/L}$ ), linear ( $r^2=0.99$ ) and accurate over the range  $0\text{-}30 \mu\text{g/L}$  for quantification of residual poly-DADMAC in treated, potable water. However, the instrument and inter-day method precision exceeded the internal limit of being  $\geq 10\%$  RSD. For potable water, there was a strong positive linear relationship between: poly-DADMAC levels and: TOC, Redox potential, and a strong negative, linear relationship between poly-DADMAC levels and PH. Future research work must consider (inter alia): (1) improvement of the instrument and inter-day precision of the colorimetric analytical

method: The observed instrument precision (%RSD ( $\pm$ SD), for Method 1 (absorbance of peak at 690 nm) and Method 2 (area of peak at 690 nm), was  $18.05 (\pm 17.65)$  and  $18.81 (\pm 18.44)$ , respectively, which exceed the typical  $\leq 10\%$  limit. The overall mean between-batch (reproducibility)% RSD was:  $54.37 (\pm 30.03)$  for Method 1,  $35.89 (\pm 34.89)$  for Method 2, and  $13.50 (\pm 12.64)$  for Method 3; (2) evaluation of the recovery at the observed LOQ: No recovery data for blank matrix or real samples, is reported in the original method [21], at spike levels less than  $10 \mu\text{g/L}$  down to  $2 \mu\text{g/L}$  of poly-DADMAC; (3) use of other organic capping agents, (e.g., tannic acid, polyvinylpyrrolidone): The current method development, and application, is based on the use of only citrate-capped gold nanoparticles; (4) efficient sample preparation methods for NOM removal from raw dam water The use of cyclodextrin polyurethanes for NOM removal was shown to achieve 10-24% NOM removal from raw water, in one South African study. The proposed use of strong base anion exchange resin, to remove most of the NOM, is one possible option; (5) transfer of this analytical to a real raw water treatment plant for application: The determination of residual poly-DADMAC in treated water is useful for at least two reasons: (1) establishment of over-dosing with the coagulant and (2) establishment of water quality compliance-health risk assessment, regarding the international allowable limit of a residual of  $\leq 50 \mu\text{g/L}$ . The initially reported method development work, and this current study, was undertaken at laboratory scale, in an academic (university), and process evaluation, setting; (6) application of this same Au-NP colorimetric method to quantification of NOM, or other organic matter, present in raw dam water: The current study has shown possible interference by NOM, present in untreated raw dam water, by its reaction with the Au-NPs, in the analysis of poly-DADMAC. NOM in natural water can be quantified using size exclusion chromatography-organic carbon detection-organic nitrogen detection (LC-OCD-OND) [40]; (7) toxicity assessment studies of residual poly-DADMAC, and disinfection by-products (DBPs): poly-DADMAC can be toxic to aquatic organisms at levels above  $50 \mu\text{g/L}$ , and has potential to form *N*-nitrosodimethylamine (NDMA), which is a disinfection by-product, and a suspected carcinogen.

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