

Contents

	Page
List of Tables	xiii
List of Figures	xvii
List of Abbreviations	xx
CHAPTER 1: Introduction	1
1.1 Introduction	1
1.2 Background	2
1.2.1 Chemical identification	2
1.2.2 Physical and chemical properties	3
1.3 Methods to evaluate fish quality	5
1.3.1 Sensory evaluation	5
1.3.2 Microbial methods	5
1.3.3 Volatile compounds	6
1.3.4 Lipid oxidation	6
1.3.5 Adenosine-5'-triphosphate (ATP)	7
1.3.6 K-value measurement	8
1.3.7 Physical measurements	8
1.4 Determination of dimethylamine and trimethylamine	8
1.4.1 Spectrophotometric detection	9
1.4.2 Sensor	10
1.4.3 Capillary electrophoresis	12
1.4.4 High performance liquid chromatography	13
1.4.5 Gas chromatography	15
1.5 Sample preparation	18
1.5.1 Liquid liquid extraction (LLE)	19
1.5.2 Headspace solvent microextraction or headspace single drop microextraction (HS-SDME)	19

Contents (Continued)

	Page
1.5.3 Solid phase extraction and derivatization	20
1.5.4 Solid phase microextraction	21
1.5.5 Static headspace	21
1.6 Objectives	22
CHAPTER 2: Experimental	23
2.1 Materials	23
2.2 Instruments and Apparatus	23
2.3 Glasswares	24
2.4 Analysis system	24
2.5 Preparation of standard solutions	25
2.5.1 DMA standard stock solution	25
2.5.2 TMA standard stock solution	26
2.5.3 DMA and TMA standard solution	26
2.6 Optimization of the GC-NPD conditions	26
2.6.1 Carrier gas flow rate	26
2.6.2 Column temperature	27
2.6.3 Other parameters	27
2.7 Optimization of headspace conditions	28
2.7.1 Equilibration time	28
2.7.2 Equilibration temperature	29
2.7.3 Sample volume (phase ratio)	29
2.7.4 Size of vial (volume)	30
2.7.5 Salt and amount of salt	30
2.8 Linear dynamic range (LDR, Linearity)	30
2.9 Limit of detection (LOD)	31
2.10 Sample Analysis	32

Contents (Continued)

	Page
2.10.1 Sampling	33
2.10.2 Sample preparation	34
2.11 Matrix Interference	34
2.12 Method validation	35
2.12.1 Recovery	35
2.12.2 Accuracy	35
2.12.3 Precision	36
2.13 Qualitative and quantitative analysis of DMA and TMA in fish and shrimp samples	37
2.13.1 Qualitative Analysis	37
2.13.2 Quantitative Analysis	37
2.13.2.1 Matrix match calibration curve	37
2.14 Quality assurance and quality control	38
CHAPTER 3: Results and Discussion	39
3.1 Optimization of the GC-NPD conditions for DMA and TMA analysis	39
3.1.1 Carrier gas flow rate	39
3.1.2 Column temperature programming	45
3.1.3 Injector temperature	52
3.1.4 Detector temperature	53
3.1.5 The fuel gas flow rate (Hydrogen gas)	55
3.1.6 Oxidant gas flow rate (air)	57
3.1.7 The split ratio	59
3.1.8 Summary of GC-NPD conditions	60
3.1.9 Headspace analysis conditions	62
3.1.10 Equilibration temperature	63

Contents (Continued)

	Page
3.1.11 Equilibration time	65
3.1.12 Sample volume (phase ratio)	67
3.1.13 Vial volume size	70
3.1.14 Salts and amount of salts	71
3.1.15 Summary of headspace conditions	74
3.2 Linear dynamic range (LDR, Linearity)	75
3.3 Limit of detection (LOD)	79
3.4 Sample Analysis	81
3.4.1 Sampling	81
3.4.2 Sample preparation	82
3.4.3 Sample size	82
3.5 Matrix Interference	84
3.6 Method validation	89
3.6.1 Accuracy and Recovery	89
3.6.2 Precision	91
3.7 Qualitative and quantitative analysis of DMA and TMA in fish and shrimp samples	92
3.7.1 Qualitative Analysis	92
3.7.2 Quantitative Analysis	93
3.7.3 The criteria for quality of fish product	97
CHAPTER 4: Conclusions	98
References	102
Vitae	115

List of Tables

Table		Page
1.1	Chemical identification of DMA and TMA	3
1.2	Physical and chemical properties of DMA and TMA	4
1.3	Application of GC to the determination of aliphatic amines	18
2.1	Optimizations of column temperature programming	27
2.2	Optimization of other parameters for the GC-NPD system	28
2.3	The information of samples	34
3.1	HETP of DMA ($100 \mu\text{g mL}^{-1}$) and TMA ($1 \mu\text{g mL}^{-1}$) standard solution at various carrier gas flow rates	44
3.2	Effect of initial temperature on the responses of DMA ($100 \mu\text{g mL}^{-1}$) and was TMA ($1 \mu\text{g mL}^{-1}$) standard solution	45
3.3	Effect of holding time at initial temperature on the responses of DMA ($100 \mu\text{g mL}^{-1}$) and TMA ($1 \mu\text{g mL}^{-1}$) standard solution	47
3.4	Effect of temperature ramp rate on the responses of DMA ($100 \mu\text{g mL}^{-1}$) and TMA ($1 \mu\text{g mL}^{-1}$) standard solution	48
3.5	Effect of final temperature on the responses of DMA ($100 \mu\text{g mL}^{-1}$) and TMA ($1 \mu\text{g mL}^{-1}$) standard solution	49
3.6	Effect of holding time at final temperature on the responses of DMA ($100 \mu\text{g mL}^{-1}$) and TMA ($1 \mu\text{g mL}^{-1}$) standard solution	50
3.7	Effect of injector temperature on the responses of DMA ($100 \mu\text{g mL}^{-1}$) and TMA ($1 \mu\text{g mL}^{-1}$) standard solution	52
3.8	Effect of detector temperature on the responses of DMA ($100 \mu\text{g mL}^{-1}$) and TMA ($1 \mu\text{g mL}^{-1}$) standard solution	54
3.9	Effect of hydrogen gas flow rate on the responses of DMA ($100 \mu\text{g mL}^{-1}$) and TMA ($1 \mu\text{g mL}^{-1}$) standard solution	57

List of Tables (Continued)

Table		Page
3.10	Effect of air flow rate on the responses of DMA (100 $\mu\text{g mL}^{-1}$) and TMA (1 $\mu\text{g mL}^{-1}$) standard solution	58
3.11	Effect of the split ratio on the responses of DMA (100 $\mu\text{g mL}^{-1}$) and TMA (1 $\mu\text{g mL}^{-1}$) standard solution	59
3.12	The optimum conditions of GC-NPD for DMA and TMA	61
3.13	Effect of equilibration temperature on the responses of DMA (100 $\mu\text{g mL}^{-1}$) and TMA (1 $\mu\text{g mL}^{-1}$) standard solution	64
3.14	Effect of equilibration time on the responses of DMA (100 $\mu\text{g mL}^{-1}$) and TMA (1 $\mu\text{g mL}^{-1}$) standard solution	66
3.15	Effect of phase ratio on the responses of DMA (100 $\mu\text{g mL}^{-1}$) and TMA (1 $\mu\text{g mL}^{-1}$) standard solution	69
3.16	Effect of size of vial volume on the responses of DMA (100 $\mu\text{g mL}^{-1}$) and TMA (1 $\mu\text{g mL}^{-1}$) standard solution	70
3.17	Effect of salt and amount of salt on the responses of DMA (150 $\mu\text{g mL}^{-1}$) standard solution	72
3.18	Effect of salt and amount of salt on the responses of TMA (1 $\mu\text{g mL}^{-1}$) standard solution	73
3.19	The optimum conditions of headspace system for DMA and TMA analysis	74
3.20	The responses of DMA at various concentrations	76
3.21	The responses of TMA at various concentrations	78
3.22	The data of the blank measurements by headspace technique, $n_B = 20$	80
3.23	The limit of detection for DMA and TMA standard solution with optimum conditions of HS-GC-NPD	81

List of Tables (Continued)

Table		Page
3.24	The information of samples	81
3.25	Effect of the sample size on the responses of DMA (25 $\mu\text{g mL}^{-1}$) and TMA (0.5 $\mu\text{g mL}^{-1}$) standard solution	83
3.26	Effect of matrix on the responses of DMA in fish and shrimp samples	85
3.27	Effect of matrix on the responses of TMA in fish and shrimp samples	86
3.28	Statistic values for the comparison between the slope for DMA standard curve and matrix match calibration curve of various seafood samples	88
3.29	Statistic values for the comparison between the slope for TMA standard curve and matrix match calibration curve of various seafood samples	88
3.30	Level of significance (<i>P</i> value) from ANOVA for the comparison between the slope the standard curve and matrix match calibration curve of various seafood samples	89
3.31	Recovery of DMA of various fish and shrimp samples at spiked concentrations of 100 and 200 $\mu\text{g mL}^{-1}$	90
3.32	Recovery of TMA of various fish and shrimp samples at spiked concentrations of 0.5 and 1 $\mu\text{g mL}^{-1}$	91
3.33	Precision of DMA of various fish and shrimp samples at spiked concentrations of 100 and 200 $\mu\text{g mL}^{-1}$	92
3.34	Precision of TMA of various fish and shrimp samples at spiked concentrations of 0.5 and 1 $\mu\text{g mL}^{-1}$	92
3.35	Amount of DMA in fish and shrimp samples by matrix match calibration curve	95

List of Tables (Continued)

Table		Page
3.36	Amount of TMA in fish and shrimp samples by matrix match calibration curve	96
4.1	Comparison between proposed method and another sample preparation methods for analysis aliphatic amines in seafood	100

List of Figures

Figure		Page
1.1	Mechanisms of trimethylamine and dimethylamine	2
2.1	Analysis system for dimethylamine and trimethylamine, (a) Headspace (b) Gas Chromatography with Nitrogen Phosphorus Detector, (HS-GC-NPD)	25
2.2	Laboratory-built water bath systems	29
2.3	Analytical procedures of DMA and TMA for fish and shrimp samples	33
3.1	The van Deemter plot	41
3.2	Measurement used in calculating total theoretical plates	43
3.3	The van Deemter plot of DMA and TMA	44
3.4	Responses of DMA ($100 \mu\text{g mL}^{-1}$) and TMA ($1 \mu\text{g mL}^{-1}$) standard solution at various initial temperatures	46
3.5	Responses of DMA ($100 \mu\text{g mL}^{-1}$) and TMA ($1 \mu\text{g mL}^{-1}$) standard solution at various holding time	47
3.6	Responses of DMA ($100 \mu\text{g mL}^{-1}$) and TMA ($1 \mu\text{g mL}^{-1}$) standard solution at various temperature ramp rates	48
3.7	Responses of DMA ($100 \mu\text{g mL}^{-1}$) and TMA ($1 \mu\text{g mL}^{-1}$) standard solution at various final temperatures	49
3.8	Responses of DMA ($100 \mu\text{g mL}^{-1}$) and TMA ($1 \mu\text{g mL}^{-1}$) standard solution at various holding time at final temperatures	51
3.9	The optimum column temperature programming for DMA and TMA analysis	51
3.10	Responses of DMA ($100 \mu\text{g mL}^{-1}$) and TMA ($1 \mu\text{g mL}^{-1}$) standard solution at various injector temperatures	53
3.11	Responses of DMA ($100 \mu\text{g mL}^{-1}$) and TMA ($1 \mu\text{g mL}^{-1}$) standard solution at various detector temperatures	55

List of Figures (Continued)

Figure		Page
3.12	Responses of DMA ($100 \mu\text{g mL}^{-1}$) and TMA ($1 \mu\text{g mL}^{-1}$) standard solution at various hydrogen gas flow rates	57
3.13	Responses of DMA ($100 \mu\text{g mL}^{-1}$) and TMA ($1 \mu\text{g mL}^{-1}$) standard solution at various air flow rates	58
3.14	Responses of DMA ($100 \mu\text{g mL}^{-1}$) and TMA ($1 \mu\text{g mL}^{-1}$) standard solution at various the split ratios	60
3.15	The chromatogram of DMA ($100 \mu\text{g mL}^{-1}$) and TMA ($1 \mu\text{g mL}^{-1}$) at optimum GC-NPD conditions	62
3.16	A headspace vial containing the volatile DMA and TMA in standard solution: V_G = volume of the gas phase, V_S = volume of the liquid sample	63
3.17	Responses of DMA ($100 \mu\text{g mL}^{-1}$) and TMA ($1 \mu\text{g mL}^{-1}$) standard solution at various equilibration temperatures	65
3.18	Responses of DMA ($100 \mu\text{g mL}^{-1}$) and TMA ($1 \mu\text{g mL}^{-1}$) standard solution at various equilibration times	66
3.19	Responses of DMA ($100 \mu\text{g mL}^{-1}$) and TMA ($1 \mu\text{g mL}^{-1}$) standard solution at various phase ratios	69
3.20	Responses of DMA ($100 \mu\text{g mL}^{-1}$) and TMA ($1 \mu\text{g mL}^{-1}$) standard solution at various size of vial volume	71
3.21	Responses of DMA ($150 \mu\text{g mL}^{-1}$) standard solution at various salt and amount of salt	73
3.22	Responses of TMA ($1 \mu\text{g mL}^{-1}$) standard solution at various salt and amount of salt	74
3.23	Chromatogram of TMA ($1 \mu\text{g mL}^{-1}$) and DMA ($100 \mu\text{g mL}^{-1}$) standard solution by HS-GC-NPD system	75
3.24	Linear dynamic range of DMA	77

List of Figures (Continued)

Figure		Page
3.25	Linear dynamic range of TMA	79
3.26	Responses of DMA ($25 \mu\text{g mL}^{-1}$) and TMA ($0.5 \mu\text{g mL}^{-1}$) standard solution at various sample size	84
3.27	Matrix match calibration curve of DMA of fish and shrimp samples	86
3.28	Matrix match calibration curve of TMA of fish and shrimp samples	87
3.29	HS-GC-NPD Chromatogram of DMA and TMA from spiked Indian mackerel sample	94