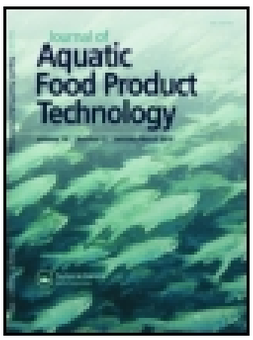


Journal of Aquatic Food Product Technology

ISSN: 1049-8850 (Print) 1547-0636 (Online) Journal homepage: http://www.tandfonline.com/loi/wafp20

Odor Evaluation of Shrimp Treated with Different Chemicals Using an Electronic Nose and a Sensory Panel

D. A. Luzuriaga PhD , F. Korel PhD & M. Ö Balaban PhD

To cite this article: D. A. Luzuriaga PhD , F. Korel PhD & M. Ö Balaban PhD (2007) Odor Evaluation of Shrimp Treated with Different Chemicals Using an Electronic Nose and a Sensory Panel, Journal of Aquatic Food Product Technology, 16:2, 57-75, DOI: 10.1300/J030v16n02_06

To link to this article: http://dx.doi.org/10.1300/J030v16n02_06

Odor Evaluation of Shrimp Treated with Different Chemicals Using an Electronic Nose and a Sensory Panel

D. A. Luzuriaga
F. Korel
M. Ö. Balaban

ABSTRACT. An electronic nose with 12 conducting polymer sensors was used to measure odors of raw shrimp treated with different chemicals. Headless shell-on pink shrimp (*Pandalus jordani*) were treated with bleach (0, 25, 50, 100 and 200 ppm), phosphates (0, 2, 4 and 6% w/v) and sulfites (0, 0.75, 1.25 and 2% w/v) and stored at 2°C for 48 hours. Odors were evaluated by sensory panels and an electronic nose. Aerobic plate counts were performed. Discriminant function analysis was used as the pattern recognition technique to differentiate samples based on odors. Results showed that the electronic nose could discriminate differences in odor due to chemicals present in shrimp. The correct classification rates

D. A. Luzuriaga, PhD, is affiliated with the Chiquita Fresh North America, SE 35th Street, Hollywood, FL 33316.

F. Korel, PhD, is affiliated with the Food Engineering Department, İzmir Institute of Technology, Urla, İzmir, 35430 Turkey.

M. Ö. Balaban, PhD, is affiliated with the Food Science and Human Nutrition Department, University of Florida, P.O. Box 110370, Gainesville, FL 32611.

Address correspondence to: M. Ö. Balaban at the above address (E-mail: mobalaban@ifas.ufl.edu).

This research was supported, in part, by the Florida Sea Grant project R/LR-Q-20.

Journal of Aquatic Food Product Technology, Vol. 16(2) 2007
Available online at http://jafpt.haworthpress.com

doi:10.1300/J030v16n02_06

for bleach, phosphate and sulfite treated shrimp were 92.7, 95.8, and 99.2%, respectively. doi:10.1300/J030v16n02_06

KEYWORDS. Shrimp, phosphates, sulfites, bleach, electronic nose, sensory, overall quality

INTRODUCTION

Shrimp is an important commodity in the United States, where its annual per capita consumption (all preparations) has increased in the last 20 years from 0.64 to 1.45 kg (U.S. Department of Commerce, 2000). Unfrozen raw shrimp has a short shelf life. During processing and commercialization, shrimp is prone to microbial deterioration. Therefore, processors try to maintain the quality of their product using different chemicals.

Shrimp melanosis (black spot) is a postmortem surface discoloration due to enzymatic browning. The endogenous shrimp enzyme polyphenol oxidase catalyzes the initial step in black spot formation (McEvily et al., 1991). Sulfiting agents have been used in shrimp since the 1950s to inhibit melanosis formation (Fieger, 1951). Some shrimp aquaculture facilities use sulfites to treat pond harvests. Detection of sulfites in shrimp is important from a food safety perspective since there is a health concern regarding asthmatics exposed to sulfites (Taylor et al., 1986).

Phosphates are used as processing aids or additives in a variety of foods. In seafood their most common use is in frozen products. They reduce thaw drip, and when used properly the retention of moisture improves texture and flavor because flavor components are not lost in the thaw drip (Finne, 1995). Use of phosphates can be abused, leading to excessive increase in water weight in raw seafood. Detection of phosphates in shrimp is not easy. Shrimp has naturally occurring phosphates, and their levels vary according to the species and harvest location. Phosphates also have strong interactions with the protein structure, which make them difficult to quantitatively extract using nondestructive solvent systems. Moreover, they can be transformed to other forms (orthophosphates) making them difficult to quantify (Finne, 1995). Therefore, alternative or indirect methods need to be developed to determine if shrimp were treated, or treated abusively with phosphates.

Another chemical that is widely used as an effective sanitizer in the food industry is bleach. Several cases have been observed where shrimp producers used bleach solutions to treat decomposed shrimp. Bleach will act as an antimicrobial and will mask the odor of decomposition. Depending on the concentration used, some residual odor of bleach can be detected. Therefore, sensors that can interact with bleach can be used to detect whether or not shrimp has been treated with it.

Sensor arrays, also known as electronic noses, have potentially wide applications in the food industry. The electronic nose has been used to detect the presence of a variety of chemicals in different products such as detection of some additives used in the sparkling wine process (Viaux et al., 1996) and detection of adulteration of peppermint oils with cheaper ingredients (Hanrieder et al., 1998). This technology was used to detect spoilage of fresh tilapia fillets treated with different concentrations of sodium lactate (Korel et al., 2001a), to detect spoilage of Alaska pink salmon (Chantarachoti et al., 2006), to determine the raw and cooked catfish quality (Korel et al., 2001b), to detect the spoilage flavors of cod roe (Jonsdottir et al., 2004) and to determine the quality of Atlantic salmon (Haugen et al., 2006). Therefore, the electronic nose can be an effective method to detect food chemicals of interest with the advantages of minimal sample preparation, no use for chemicals, fast results and ease of analysis.

The overall objective of this study was to determine the ability of an electronic nose and sensory panels to detect if shell-on pink shrimp was treated with sodium hypochlorite (bleach), sodium tripolyphosphate (phosphates) or sodium metabisulfite (sulfites). The specific objectives were (1) to treat shrimp with different levels of these chemicals and measure the electronic nose sensor response at 0, 24 and 48 hours after treatment; (2) to conduct an odor sensory panel to determine if panelists can detect the presence of these chemicals in treated shrimp; and (3) to measure microbial loads, ammonia levels, moisture content, water activity (a_w) and pH of treated shrimp during 48 hours storage to evaluate changes in shrimp odor other than those caused by the chemical treatments.

MATERIALS AND METHODS

Shrimp Samples

Three batches (8.8 kg each) of frozen pink shrimp (*Pandalus jordani*) were purchased from Lombardi's Seafood (Orlando, FL). Each batch

was split in half (4.4 kg) to replicate the study. The first batch of headless shell-on pink shrimp with 11.8/13.6 tail count/kg was treated with bleach solutions. The second batch (16.4/18.2 tail count/kg) was treated with phosphate solutions. The third batch (9.5/11.4 tail count/kg) was treated with sulfite solutions. Samples were thawed under running tap water, treated with different solutions, and stored at refrigeration temperature (2°C) for 48 hours. Control samples were untreated shrimp. Each treatment solution was prepared to have a solution:shrimp ratio as 2:1 by weight. Samples were evaluated every 24 hours for differences in odor by sensory panelists and an electronic nose. The replicate study was performed immediately after finishing the first series of experiments.

Chemicals Used and Sample Treatments

Shrimp were dipped for 10 min in bleach solutions (25, 50, 100 and 200 ppm) prepared with distilled water from a concentrated sodium hypochlorite solution (5.25% w/v).

Phosphate solutions (2, 4 and 6% w/v) were prepared from sodium tripolyphosphate (85%, Acros Organics, NJ) and distilled water. Solutions were prepared the day before and stored in sealed glass volumetric flasks at 2°C. Shrimp were dipped in cold phosphate solution for 1 hour. Phosphate solutions were cold to prevent microbial proliferation in the shrimp samples. Currently, shrimp processors use 2% and 4% phosphate solutions dips to treat shrimp.

Sulfite solutions (0.75, 1.25 and 2% w/v) were prepared from sodium metabisulfite (97%, Acros Organics, NJ) and distilled water. Shrimp were dipped in the solutions for 1 min. Present regulations for the treatment of shrimp are 1 min dip into a 1.25% sodium metabisulfite solution (Federal Register, 1982).

Samples treated with different chemicals were drained by placing them in a strainer for 3 min. Then they were placed in 1 gallon freezer Ziploc® bags and stored in a refrigerator at 2°C.

Moisture Content, Water Activity and pH Measurements

Moisture content was measured in triplicate at days 1 and 3 using the oven method (method no. 24.003, AOAC, 1980). A 50 g sample of shell-on shrimp (approximately 4 shrimp) was chopped in a chopper. Moisture content was reported as percent wet basis.

Rotronic Hygroscop DT (Rotronic, Huntington, NY) was used to measure a_w. A 5 g piece of the chopped shrimp was placed in a plastic cup provided by Rotronic and placed in the a_w meter. The temperature at which a_w was measured was 24.5 ± 0.5°C.

For pH measurements, a 20 g sample was placed in a blender with 80 ml of distilled water. The sample was blended for 15 sec, transferred to a 140 ml beaker and placed on a stirrer plate. The pH electrode (ROSS pH electrode, Model 81-02, Orion Research Inc., Beverly, MA) was connected to an Expanded Ion Analyzer. Measurements were done in duplicate.

Microbial Analysis

Aerobic plate counts were performed daily on all shrimp samples using aerobic plate count Petri film (3M Company, St. Paul, MN). Dilutions were made using pre-filled sterile disposable diluent bottles of phosphate buffer (NutraMax Products, Inc., Gloucester, MA). Petri films were incubated at 32°C/48 hours (method no. 986.33, AOAC, 2000). Colonies were counted and reported as log cfu/g of shrimp.

Ammonia Analysis

Ammonia levels in the shrimp samples were measured with an ion-selective electrode (Model 95-12, Orion Research, Inc., Boston, MA) connected to an Expanded Ion Analyzer (EA 920, Orion Research Inc., Beverly, MA). Two samples were measured for ammonia immediately after the electronic nose evaluation. The 60 g replicates were sprayed with 4 ml of 5N NaOH and analyzed for ammonia in the headspace of an air-tight box following the procedure described by Luzuriaga et al. (1997). The ammonia electrode was calibrated before, and during the experiments using 10, 100 and 1000 ppm ammonia solutions. Ammonia levels in shrimp were reported as ppm. Ammonia was only measured for the phosphate and sulfite treated shrimp.

Electronic Nose Measurements

An electronic nose (e-NOSE 4000 model, EEV Inc., Amsford, NJ) equipped with 12 conducting polymer sensors (sensor types: 483, 478, 464, 463, 462, 461, 460, 459, 458, 401, 298 and 297) was used to quantify the sensor responses to differences in odor of shrimp samples that were treated with different levels of chemicals. Electronic nose measurements

were completed at 0, 24 and 48 hours after treatment. Five replicates were analyzed by the electronic nose for each treatment. Replicates were taken at random from the plastic bags where shrimp were stored. Each replicate of about 50 g (4 headless shell-on shrimp) was taken out of the cooler 50 min before the analysis to let the shrimp equilibrate to room temperature (23°C). The day the experiment started, the electronic nose was calibrated following the manufacturers recommendation using a 75% v/v propylene glycol solution (100% solution from Fisher Scientific, No. P-355-20, Fair Lawn, NJ). The sample was put in a 140 ml beaker and placed in the sampling vessel of the electronic nose. For each replicate, the vessel was purged with compressed air for 2 min to eliminate any extraneous odor. Then the sensor head was purged for 4 min with compressed air. During 4 min purge, the sample volatiles were equilibrating in the headspace of the vessel. Sensor response data were acquired for 4 min. Analysis time for each sample took 10 min. Readings at 4 min exposure of the sensors to the samples were used for data analysis.

Sensory Evaluation

The odor of raw treated shrimp was evaluated by a 12-member sensory panel consisting of students aged 22-35 from the Food Science and Human Nutrition Department at the University of Florida. They were chosen among the seafood program students who were frequent shrimp eaters and willing to participate to the panel. The shrimp samples, approximately 50 g, were served to the panel in an opaque disposable plastic cup (125 ml) covered with a plastic lid. A "difference from control" test was performed every day during the three days of the study. After opening the lids, panelists evaluated the odor by sniffing. They were asked to record the differences in odor among the treated samples and the control (untreated shrimp). Panelists were asked to smell shrimp samples and detect if there was a difference in odor among the treated samples and the control (untreated shrimp). Panelists measured the differences on a 100 mm scale (0 mm = no difference, 100 mm = very different) (Meilgaard et al., 1999). The samples were randomized and a hidden control was included in the test. The samples were coded with three digit random numbers. At each sampling day, a random sample was taken out of the refrigerator 30 min before the sensory analysis. All panelists smelled the same samples in daylight laboratory conditions. Sensory tests were carried out for both replicates.

Data Analysis

Moisture content, microbial counts, ammonia level and sensory data were analyzed using analysis of variance of the general linear procedures (Proc GLM) of SAS software and the LSMEANS procedure for generating standard errors of the mean (SEM) (SAS, 1998). Any significant differences were analyzed by the multiple comparison procedure of Duncan's Multiple Range test, using a level of significance of $\alpha = 0.05$. Interaction between replications was tested for significance ($p < 0.05$).

Sensor readings were analyzed in Statistica for Windows (StatSoft Inc., Tulsa, OK) using discriminant function analysis (DFA) as reported by other researchers (Corcoran, 1993; Gardner and Hines, 1997; Gardner and Bartlett, 1992; Gardner and Hines, 1997). DFA was used to construct predictive functions to help in classifying sensor data based on the concentration of the chemicals used. The 12 sensor outputs were reduced to 2 discriminant functions. These functions were used to map the data in two dimensional plots and observe separation between groups. Correct classification rates and the coefficients for each function were calculated.

RESULTS AND DISCUSSION

Moisture Content, Water Activity and pH Measurements

Moisture content of shrimp did not change throughout 48 hours of storage for each batch of shrimp. Also, moisture content change owing to the different levels of chemical treatments and storage time was not significant. However, moisture content of the samples treated with bleach was significantly different from the batches treated with phosphates and sulfites ($p < 0.05$). The moisture contents of the control samples for each treatment were not significantly different from the samples treated with chemicals. The batches treated with bleach, phosphate and sulfites had average moisture contents of 75.97, 80.00 and 79.30%, respectively.

The water activity for treated shrimp showed minimal changes through out storage and within treatments. However, water activity determined for the three different batches of shrimp were slightly different. On average, the batch of shrimp treated with sulfites had the lowest water activity (0.988), bleach had 0.990, whereas the one treated with phosphates had a higher water activity (0.993). As the differences in moisture content and water activity were minimal, it was expected that the difference in

electronic nose sensors profiles will be owing to volatile components present in the sample, rather than to differences in water vapor.

pH of shrimp slightly increased throughout storage from 7.3 to 7.6 for all treatments. There were some differences in the pH among the different levels of chemicals used within each replicate. However, changes were minimal and did not follow any specific trend (data not shown). Therefore, it was assumed that variations in pH at any given sampling time were owing to natural variation of the shrimp tissue.

Microbial Analysis

The microflora present in the shrimp proliferated during storage as shown in Table 1. In general the microbial count increased by two to three log cycles during 48 hours of storage. ANOVA was performed for each chemical, for each analysis time (0, 24 and 48 hours) and for each

TABLE 1. Aerobic plate counts of shell-on pink shrimp treated with different levels of bleach, phosphates and sulfites.

Chemical Concentration		Microbial Load (log cfu/g of shrimp)		
		0 hours	24 hours	48 hours
Bleach (ppm)	Control (0)	4.60 ± 0.17^{a}	5.44 ± 0.18^{a}	8.20 ± 0.26^{b}
	25	4.60 ± 0.16^{a}	5.41 ± 0.18^{a}	8.24 ± 0.29^{b}
	50	4.74 ± 0.18^{a}	5.05 ± 0.11^{a}	7.95 ± 0.02^{b}
	100	4.50 ± 0.21^{a}	5.05 ± 0.09^{a}	7.81 ± 0.43^{b}
	200	4.42 ± 0.20^{a}	4.79 ± 0.30^{a}	7.70 ± 0.12^{b}
Phosphates (% w/v)	Control (0)	6.00 ± 0.10^{a}	$6.86 \pm 0.03^{b,x}$	6.92 ± 0.16^{b}
	2.0	5.46 ± 0.16	5.59 ± 0.20^{y}	6.47 ± 0.30
	4.0	5.35 ± 0.04	5.94 ± 0.01^{y}	6.45 ± 0.30
	6.0	5.72 ± 0.12	5.65 ± 0.11^{y}	6.30 ± 0.09
Sulfites (% w/v)	Control (0)	$5.94 \pm 0.018^{a,x}$	$7.23 \pm 0.04^{b,x}$	$7.77 \pm 0.06^{c,x}$
	0.75	$5.89 \pm 0.01^{a,w}$	$7.18 \pm 0.04^{b,x}$	$7.35 \pm 0.04^{b,w}$
	1.25	$5.82 \pm 0.03^{a,y}$	$7.07 \pm 0.08^{b,x}$	$7.17 \pm 0.03^{b,y}$
	2.0	$5.78 \pm 0.03^{a,z}$	$6.85 \pm 0.07^{b,y}$	$6.94 \pm 0.23^{b,z}$

[a-b]Superscripts in each row within each chemical treatment and concentration denote significant difference at the $p < 0.05$.

[x-z]Superscripts in each column within each chemical treatment denote significant difference at the $p < 0.05$.

replicate to see if there was any significant difference in microbial counts due to the level of the chemicals used for treatment. It was expected that bleach would have a significant effect on the bacterial load of shrimp. However, results were not significant (Table 1), meaning that the control sample had the same microbial load as shrimp treated with bleach. In the case of phosphates, at 0 and 48 hours there was no significant difference in the microbial loads due to the treatment with phosphate solutions. However, the microbial load of the control sample at 24 hours after treatment was significantly lower than that of the treated shrimp (Table 1). Even though phosphate solutions are reported to have an antimicrobial effect (Lindsay, 1985; Finne, 1995), results from this study did not corroborate this. When shrimp was treated with sulfites, there were some changes in microbial counts. Immediately after treatment, shrimp treated with 1.25 and 2.0% sulfite solutions had lower microbial loads than the 0.75% treatment and the control. After 24 hours of treatment, there was no significant difference in the microbial counts due to sulfite treatment ($p < 0.05$). However, after 48 hours, control samples had significantly higher microbial counts than the treated shrimp.

Ammonia Analysis

Ammonia levels correlated well with microbial loads. As microbial loads increased, ammonia levels increased (Table 2). In phosphate treated shrimp, there was no significant difference in ammonia levels among the levels of phosphated samples ($p < 0.05$). However, there was a significant difference between ammonia levels of samples within the same concentration at each storage time. The sulfite treated shrimp showed a clear trend of decreasing ammonia levels with an increase in sulfite concentration. Concentration of the chemicals and storage time had significant effects on the ammonia levels of the samples treated with sulfites ($p < 0.05$).

Sensory Evaluation

Sensory data showed that in general panelists had difficulty differentiating the odor of treated shrimp from that of the control samples. Throughout the study, panelists mentioned that most of the samples had similar odors. In some cases they were able to detect differences in odor of the highest levels of chemical treatment compared to the control (Table 3). In the case of bleach treated shrimp, immediately after treatment, panelists could detect differences in odor for the samples treated with 100 and 200 ppm bleach, which could be owing to the odor of the high

TABLE 2. Ammonia levels of shell-on pink shrimp treated with different levels of phosphates and sulfites.

Chemical	Concentration	Ammonia (ppm)		
		0 hrs	24 hrs	48 hrs
Phosphates (% w/v)	Control (0)	51.50 ± 5.66^{a}	70.25 ± 8.13^{b}	80.50 ± 3.77^{b}
	2.0	52.00 ± 2.59^{a}	65.75 ± 3.18^{a}	85.75 ± 3.65^{b}
	4.0	48.25 ± 6.48^{a}	$67.75 \pm 2.95^{a,b}$	80.75 ± 4.36^{b}
	6.0	53.75 ± 5.31^{a}	$70.50 \pm 2.83^{a,b}$	81.75 ± 5.07^{b}
Sulfites (% w/v)	Control (0)	$151.25 \pm 1.77^{a,x}$	$274.50 \pm 14.38^{b,x}$	$335.00 \pm 47.14^{b,x}$
	0.75	$159.50 \pm 18.38^{a,x}$	$251.75 \pm 8.13^{b,x}$	$270.75 \pm 6.25^{b,x}$
	1.25	$123.80 \pm 23.38^{x,y}$	$223.50 \pm 23.57^{x,y}$	203.0 ± 26.40^{y}
	2.0	$91.65 \pm 7.47^{a,y}$	$179.25 \pm 14.97^{b,y}$	$196.25 \pm 19.21^{b,y}$

$^{a\text{-}b}$Superscripts in each row within each chemical treatment and concentration denote significant difference at the $p < 0.05$.

$^{x\text{-}y}$Superscripts in each column within each chemical treatment denote significant difference at the $p < 0.05$.

concentrations of bleach applied to the samples. After 24 hours they could not detect any differences, but after 48 hours the sample treated with 200 ppm bleach had a significantly different odor from that of control, which could be related to the lower microbial load in those samples ($p < 0.05$).

Sensory results for shrimp treated with phosphate were unexpected (Table 3). Since sodium tripolyphosphate is not a volatile compound, it was anticipated that panelists would not be able to detect differences from the control. However, immediately after treatment, panelists detected differences in odor of the 6% phosphate treated shrimp compared to control. In general, sensory data for phosphate treated samples had lower scores compared to bleach or sulfite treated shrimp, meaning that odors from phosphate treated shrimp were closer to that of control.

Panelists could not detect major differences in sulfite treated shrimp (Table 3). However, there was a significant difference between the control and 2% sulfite treated shrimp at 0 hour ($p < 0.05$). The 1.25% sulfite treated shrimp at 48 hours of storage was significantly different than the samples at 0 and 24 hours ($p < 0.05$). All other samples and storage times did not show significant differences in the odor of treated shrimp versus that of the control.

TABLE 3. Average sensory score given by the 12 panelists to shell-on pink shrimp treated with different chemicals.

Chemical Concentration		Sensory Scores		
		0 hrs	24 hrs	48 hrs
Bleach (ppm)	Control (0)	12.38^{x}	15.34	17.50^{x}
	25	14.05^{x}	16.17	14.04^{x}
	50	13.09^{x}	21.17	23.13^{x}
	100	39.42^{y}	16.59	16.71^{x}
	200	48.96^{a,y}	27.54^{b}	39.50^{ab,y}
Phosphates (% w/v)	Control (0)	6.82^{x}	8.17	8.17
	2	8.62^{xy}	9.46	10.79
	4	11.15^{y}	11.84	11.88
	6	16.67^{z}	16.46	17.13
Sulfites (% w/v)	Control (0)	19.84^{x}	28.63	12.96
	0.75	31.30^{xy}	20.75	14.05
	1.25	31.13^{a,xy}	32.59^{a}	15.09^{b}
	2.0	43.84^{y}	29.84	22.25

$^{a-b}$: Superscripts in each row within each chemical treatment and concentration denote significant difference at the $p < 0.05$.

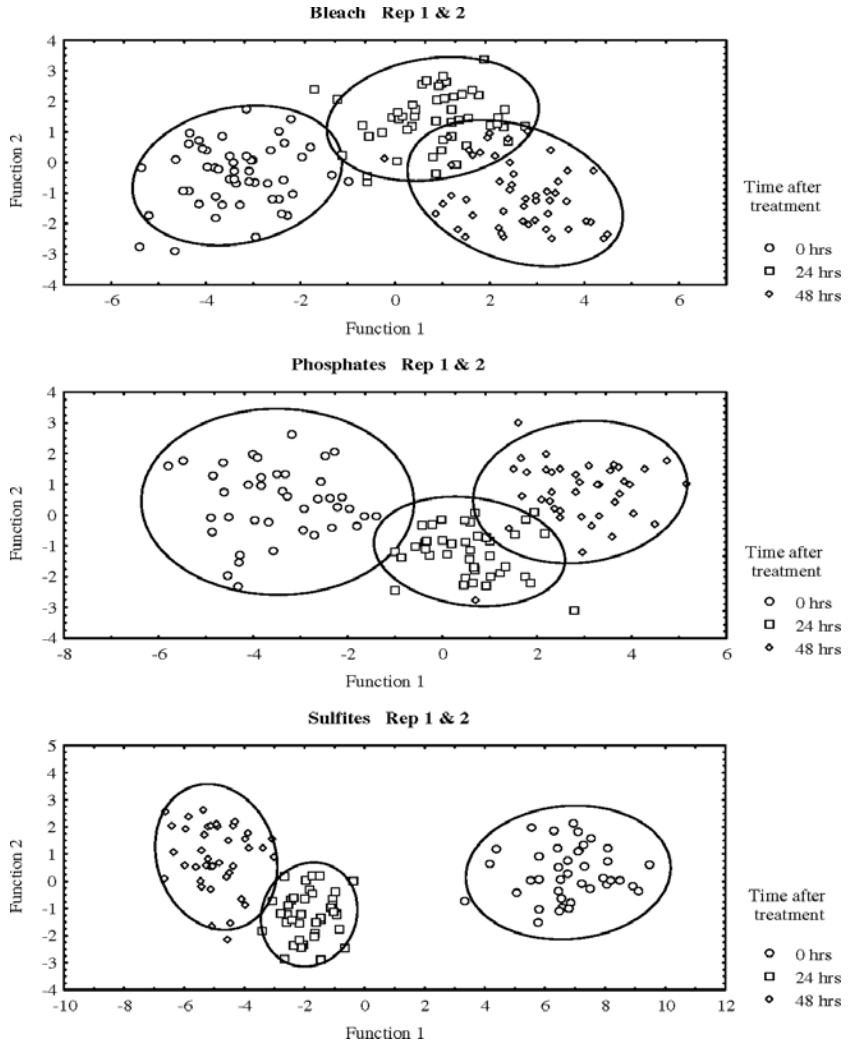
$^{x-z}$: Superscripts in each column within each chemical treatment denote significant difference at the $p < 0.05$.

Sensory score 0 means no difference, 100 means very different from the control.

Electronic Nose Measurements

Electronic nose sensor data analyzed with DFA showed very good classification for shrimp treated with the three chemicals. Based on the results from physical, chemical and microbial data, it was concluded that electronic nose sensor data should be analyzed separately for every analysis time (0, 24 and 48 hours) and for each replicate. Replicates for each analysis time were also combined to observe the degree of classification on pooled data. Microbial numbers were changing during storage, and these could result in changes in the odor of shrimp, which was demonstrated by the DFA on electronic nose sensor data. Figure 1 shows the classification of sensor data for each analysis time. For all three chemicals, the classification of sensor data in all analysis times (0, 24 and 48 hours) was very good. The overall correct classification rates for bleach, phosphate and sulfite treated shrimp were 92.7, 95.8 and 99.2%, respectively. These data show that

FIGURE 1. DFA of electronic nose readings of shrimp treated with different chemicals, grouped by storage time at 2°C.



the electronic nose was able to sense differences in odor at 0, 24 and 48 hours. Since data were pooled together for both replicates, it can be concluded that shrimp odors in both replicates were similar, otherwise data would have been more dispersed and with lower classification rates.

DFA for each chemical at each time step and for each replicate showed high classification rates when sensor data were classified by the concentration of chemical used. Shrimp that was treated with bleach had classification rates ranging from 92 to 100%. Phosphate treated shrimp had classification rates of 95-100%, whereas that of sulfite-treated shrimp ranged from 90 to 100%. These results demonstrate that DFA of sensor data can detect differences in shrimp treated with different levels of these three chemicals.

The DFA results for the bleach-treated shrimp for replicate 1 are shown in Figure 2. Clusters are well formed with minimum overlap. Since microbial loads were not significantly different among the treatments, it is expected that discrimination was due to the odor of the bleach on the shrimp. The coefficients of the discriminant functions for replicate 1 are given in Table 4.

In the phosphate treated shrimp, Figure 3 showed good separation of clusters for each level of treatment for replicate 1. The coefficients for the discriminant functions for replicate 1 are listed in Table 4. Some overlap existed; however, classification rates were above 95%. Discrimination of the different levels of phosphate treated shrimp was not expected, since sodium tripolyphosphate is not volatile. Some of the differences in odor detected by the electronic nose could be due to the ability to bind water or to chelate metal ions. These could affect the rate of formation or volatilization of other compounds in the shrimp, which were detected by the electronic nose sensors and to some degree by the panelists.

The sulfite treated shrimp (Figure 4) showed distinct clusters for each level of sulfite. Table 4 shows the coefficients of the discriminant functions. Classification rates were lower compared to the other two chemicals, and some overlap was expected. In sulfite treated shrimp, ammonia levels were different for different levels of sulfite. Therefore, it is expected that lower classification rates could be due to the differences in ammonia levels. The nose responded to the ammonia and the odor profiles changed slightly. The data for replicate 2 and combined replicates for all shrimp samples, treated with different chemicals, had similar trends and was not given here.

FIGURE 2. DFA of electronic nose readings of shrimp stored over time, grouped by concentration of bleach solution (for rep 1).

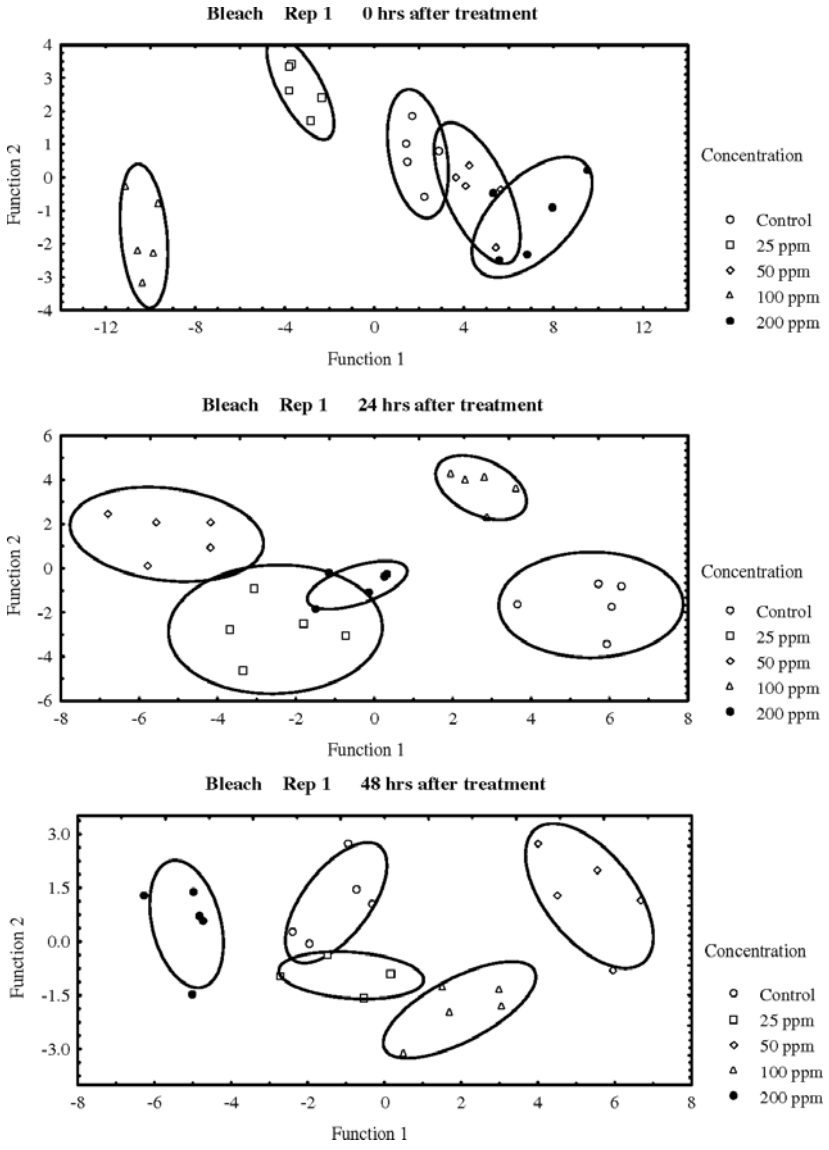


TABLE 4. Coefficients for DFA functions correlating electronic nose sensor readings to chemical concentration.

Chemicals	Rep	Time after treatment (hrs)	DFA function	Coefficients (T_n = electronic nose sensor type)												
				T_{401}	T_{298}	T_{297}	T_{483}	T_{478}	T_{464}	T_{463}	T_{462}	T_{461}	T_{460}	T_{459}	T_{458}	Constant
Bleach	1	Control (0)	1	−52.82	3.65	−4.01	41.42	−6.02	−26.53	−41.65	130.08	21.57	36.91	−52.64	−18.95	−16.14
			2	−21.41	−9.64	31.32	5.74	−57.08	−12.04	4.25	15.73	3.42	41.22	−32.99	−30.91	33.39
		24	1	20.22	16.63	0.57	9.85	−21.72	−2.02	23.17	−59.00	−10.46	−10.79	−14.09	−12.51	36.22
			2	−108.60	10.92	10.04	4.07	−106.22	−13.97	36.58	−2.31	35.49	4.19	−23.93	16.17	87.09
		48	1	6.96	11.08	−0.28	6.11	−74.10	14.70	10.42	−61.99	19.05	7.14	−16.94	−2.07	10.86
			2	−10.69	7.45	−7.96	−16.63	15.65	21.74	−0.25	−1.52	−49.02	−4.06	3.28	27.17	−28.14
Phosphates	1	Control (0)	1	−28.31	−25.48	30.19	−14.22	58.46	−15.53	−5.72	72.81	−67.44	−8.21	12.43	42.64	31.88
			2	−38.84	−8.89	11.65	2.10	15.10	−16.26	14.70	19.50	−12.07	−9.03	−24.99	49.88	21.31
		24	1	121.47	18.02	−47.46	14.81	14.48	37.89	−56.42	6.14	46.23	−5.73	−16.78	−61.71	−19.11
			2	174.09	4.26	−31.03	1.39	90.69	−11.26	0.45	−64.18	92.44	18.29	−135.81	−11.73	−28.47
		48	1	−25.31	−16.50	−8.94	−4.55	30.31	0.09	−33.21	62.19	−92.63	57.93	78.19	25.27	−133.73
			2	−17.95	−9.14	−6.67	9.18	18.66	12.16	−13.79	11.70	−35.01	16.93	8.98	14.86	−34.30
Sulfites	1	Control (0)	1	15.66	6.57	−1.40	5.92	6.97	13.82	−3.80	−20.37	−9.70	−5.45	−4.43	−15.25	−54.89
			2	−23.75	−3.36	5.60	−3.20	−35.44	3.21	−7.19	15.14	7.36	−18.27	59.26	−10.33	17.66
		24	1	80.26	−34.13	5.95	−31.01	171.91	−9.30	−9.77	43.50	−133.09	−63.90	145.92	27.81	−63.45
			2	−24.55	0.42	−6.95	−2.22	66.77	2.43	13.85	−15.85	−55.40	−21.80	31.92	25.38	−32.56
		48	1	−86.73	5.38	16.72	−6.27	77.36	−47.59	69.16	−29.91	−37.34	8.35	−65.14	47.03	98.77
			2	−32.73	2.86	7.46	−17.61	90.12	−32.16	40.62	−15.86	−27.47	−17.12	14.44	8.78	23.60

FIGURE 3. DFA of electronic nose readings of shrimp stored over time, grouped by concentration of phosphates solution (for rep 1).

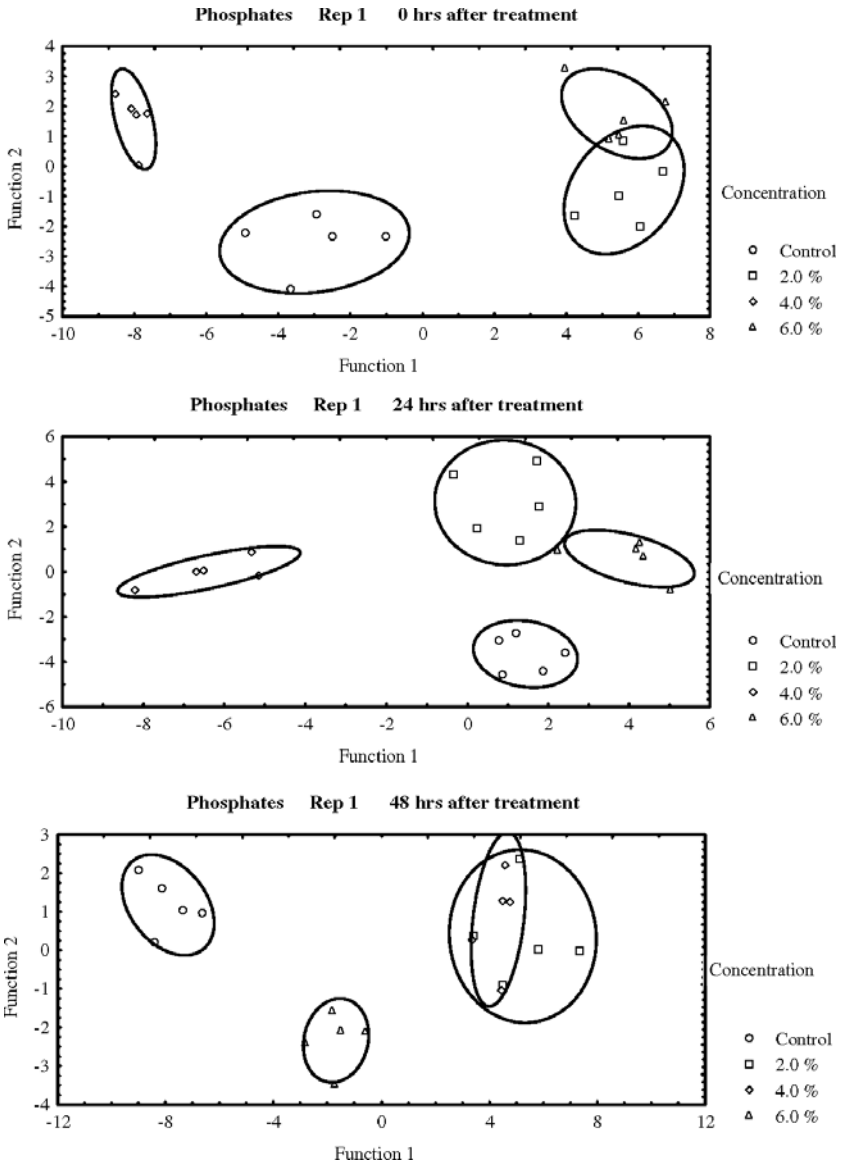
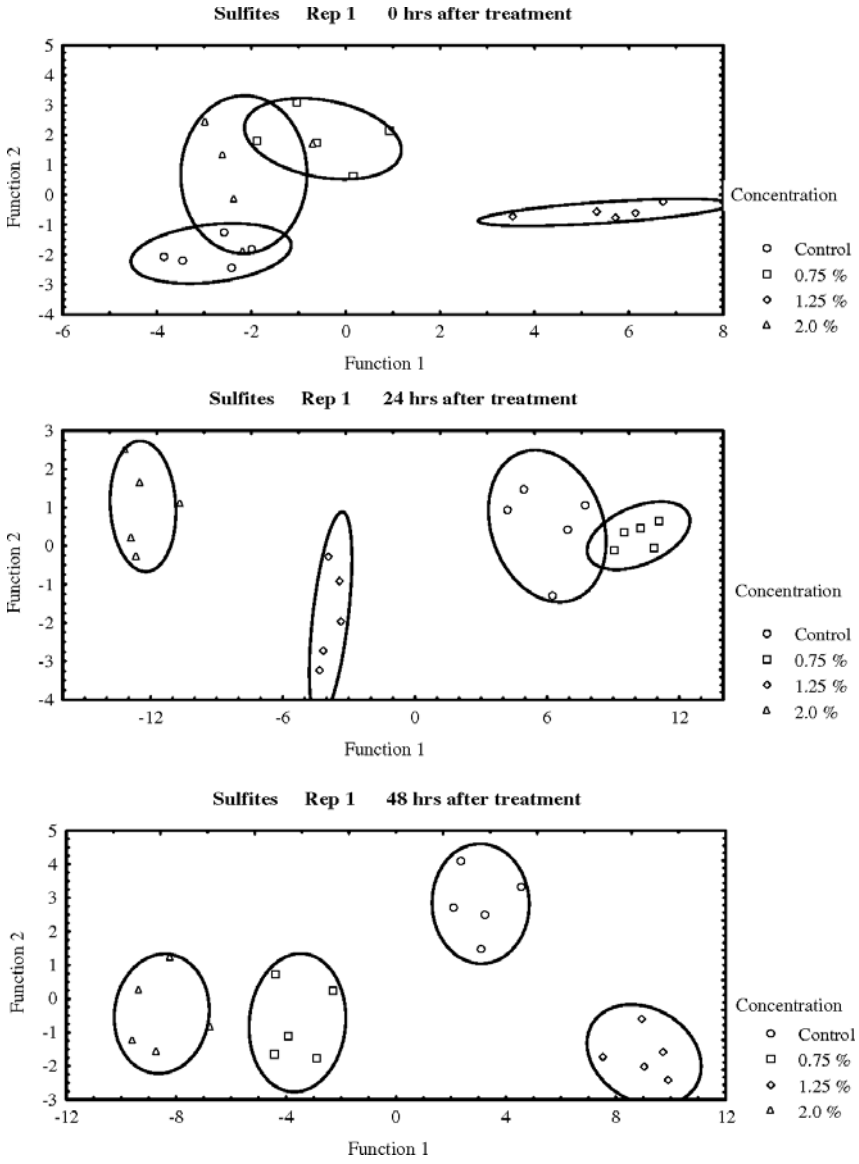


FIGURE 4. DFA of electronic nose readings of shrimp stored over time, grouped by concentration of sulfites solution (for rep 1).



CONCLUSIONS

This study concluded that panelists had difficulty determining if shrimp was treated with a chemical, basing their judgments on odor alone. However, the electronic nose sensors showed the ability to discriminate samples of shrimp treated with different levels of chemicals under the conditions described here. The electronic nose also detected the change in shrimp odor after 24 and 48 hours of storage. From the results it could be concluded that the changes in odor due to storage are more pronounced than that of the chemical treatments. The electronic nose could be an effective alternative method to detect the presence of sulfites, phosphates and bleach in shrimp. However, more data should be gathered to take into account odor differences due to shrimp harvesting locations, different species, processing conditions, storage conditions, etc. More samples will bring more variability to the odor, and probably will lower classification rates for the detection of these chemicals. In this study only DFA was used as the pattern recognition technique. Other techniques could be used to obtain better discrimination, making this technology a fast, simple and objective method to detect treated shrimp, and this can be implemented by seafood buyers, processing facilities and inspection agencies.

REFERENCES

AOAC. 1980. Official Methods of Analysis. 13th edition. Association of Official Analytical Chemists, Inc., Washington, DC.

AOAC. 2000. Official Method 986.33. Official Methods of analysis of AOAC International. 17th edition. AOAC International, Gaithersburg, MD.

Bartlett, P.N., Elliot, J.M., and Gardner, J.W. 1997. Electronic noses and their application in the food industry. Food Technol. 51(12): 44-48.

Chantarachoti, J., Oliveira, A.C.M., Himelbloom, B.H., Crapo, C.A., and McLachlan, D.G. 2006. Portable electronic nose for detection of spoiling Alaska pink salmon (*Oncorhynchus gorbuscha*). J. Food Sci. 71(5): S414-S421.

Corcoran, P. 1993. Electronic odour sensing systems. Electron. Commun. Eng. J. 5(5): 303-308.

Federal Register. 1982. Sulfiting agents: Proposed affirmation of GRAS status with specific limitations. 41: 29956. U.S. Government. Washington, DC.

Fieger, E.A. 1951. Cause and prevention of blackspot on shrimp. Ice and Refrig. 120: 49-50.

Finne, G. 1995. Phosphates: Production aids for food processors. SCOPE, a Technical Bulletin from Silliker Laboratories. Chicago Heights, IL. January, pp. 1-5.

Gardner, J.W. and Bartlett, P.N. 1992. Pattern recognition in odour sensing. In: Gardner, J.W., Bartlett, P.N., editors. Sensors and Sensory Systems for an Electronic Nose. Kluwer, NATO ASI Series: Dordrecht, The Netherlands. pp. 161-180.

Gardner, J.W. and Hines, E.L. 1997. Pattern analysis techniques. In: Kress-Rogers E., editor. Handbook of Biosensors and Electronic Noses. Medicine, Food, and the Environment. CRC Press, Inc., Boca Raton, FL. pp. 633-652.

Hanrieder, D., Lauer, F., and Hirschfelder, M. 1998. Investigations on peppermint oils using electronic noses. Proc. 5th Int. Symp.Olfaction and Electronic Nose. Sept. 27-30, 1998. Hunt Valley, MA.

Haugen, J.E., Chanie, E., Westad, F., Jonsdottir, R., Bazzo, S., Labreche, S., Marcq, P., Lundby, F., and Olafsdottir, G. 2006. Rapid control of smoked Atlantic salmon (*Salmo salar*) quality by electronic nose: Correlation with classical evaluation methods. Sens. Actu. B 116: 72-77.

Hodgins, D. 1997. The electronic nose: Sensor array-based instruments that emulate the human nose. In: Marsili, R., editor. Techniques for Analyzing Food Aroma. Marcel Dekker, Inc. New York, NY. pp. 331-371.

Jonsdottir, R., Olafsdottir, G., Martinsdottir, E., and Stefansson, G. 2004. Flavor characterization of ripened cod roe by gas chromatography, sensory analysis, and electronic nose. J. Agric. Food Chem. 52: 6250-6256.

Korel, F., Luzuriaga, D.A., and Balaban, M.O. 2001a. Quality assessment of tilapia (*Oreochromis niloticus*) fillets treated with sodium lactate using electronic nose and machine vision. J. Food Sci. 66(7): 1018-1024.

Korel, F., Luzuriaga, D.A., and Balaban, M.O. 2001b. Quality evaluation of raw and cooked catfish fillets : Use of electronic nose and machine vision. J. Aquatic Food Prod. Technol. 10(1): 3-18.

Lindsay, R.C. 1985. Food additives. In: Food Chemistry. Second Edition. Fennema, O.R., editor. Marcel Dekker, Inc. New York, NY. pp. 629-687.

Luzuriaga, D.A., Balaban, M.O., and Hasan, R. 1997. Automated headspace ammonia analysis of shrimp. J. Aquatic Food Process Technol. 6(3): 29-52.

McEvily, A.J., Iyengar, R., and Otwell, S. 1991. Sulfite alternative prevents shrimp melanosis. Food Technol. 9: 80-86.

Meilgaard, M., Civille, G.V., and Carr, B.T. 1999. Sensory Evaluation Techniques. CRC Press, New York, NY.

SAS. 1998. Statistical Analysis Systems. User's Guide: Statistics. SAS Institute. Cary, NC.

Shurmer, H.V. 1990. An electronic nose: A sensitive and discriminating substitute for an mammalian olfactory system. IEEE Proc. 137-G(3): 197-204.

Taylor, S.L., Higley, N.A., and Bush, R.K. 1986. Sulfites in foods. Uses, analytical methods, residues, fate, exposure assessment, metabolism, toxicity, and hypersensitivity. Adv. Food Res. 30: 1-76.

U.S. Department of Commerce. 2000. Fisheries of the United States, 2000. Current Fishery Statistics. Silver Spring, MD.

Viaux, L., Magne, V., and Robillard, B. 1996. The electronic nose to help determination of the technical specifications of some additives and technological aids used in the sparkling wine process. Proceedings of the 3rd International Symposium on Olfaction and Electronic Nose. Nov. 3-6, 1996. Miami, FL.

doi:10.1300/J030v16n02_06