The synthesis of vanillin - learning about aspects of sustainable chemistry by comparing different syntheses

La síntesis de la vainilla - aprendiendo sobre aspectos de química sostenible mediante la comparación de diferentes síntesis

Nicole Garner[1], Antje Siol[2], Ingo Eilks[1]

[1] Institute for Science Education, University of Bremen, [2] Center for Environmental Research and Sustainable Technology, University of Bremen, Germany, ngarner@uni-bremen.de

Abstract

This paper discusses one way of integrating the aspects of sustainable chemistry into secondary and undergraduate chemistry education. Two different synthesis reactions for vanillin are presented, which both use isoeugenol as the starting reagent. Whereas the first synthesis is performed using conventional chemistry techniques, second approach employs strategies inspired by sustainable chemistry. The discussion covers how comparison of these two experiments can aid in learning about selected sustainable chemistry principles.

Key words: *education for sustainable development, chemistry education, green chemistry, vanillin*

Resumen

Este artículo analiza una manera de integrar los aspectos de la química sostenible en la escuela secundaria y en bachillerato. Dos diferentes síntesis son presentadas, las dos usan isoeugenol como reactivo principiante (starting reagent). Mientras la primera síntesis se efectúa usando técnicas químicas convencionales, el segundo enfoque usa estrategias inspiradas por la química sostenible. La discusión abarca como la comparación de estos dos experimentos puede fomentar el aprendizaje sobre principios escogidos de química sostenible en la escuela secundaria y en bachillerato.

Palabras clave: *educación, desarrollo sostenible , educación química, química verde, vainilla*

INTRODUCTION

Economic prosperity and human welfare are challenges faced by every society. Economic prosperity has often been suggested as one of the key prerequisites for improving the quality of life. Chemistry plays a central role in this (Bradley, 2005). But economic growth can also cause environmental problems. The idea of sustainable development was born in response to limited resources and growing environmental problems. It was defined as "*development that meets the needs of the present without compromising the ability of future generations to meet their own needs.*" (World Commission on Environment and Development, 1987, p. 11). In 1992, the United Nations defined sustainability and sustainable development as normative, guiding principles for the international community, the world economy, global civil society, and politics (UNCED, 1992).

Chemical research and industry are heavily involved in the development of modern technologies and economies (Fisher, 2012). The chemical industry has contributed significantly to economic prosperity in the past, but all too often results in problems with overall resource consumption and environmental pollution. It is clear today that chemical research and industry bear the responsibility of addressing these problems. Emissions need to be reduced and the efficient use of both energy and raw materials must be maximized. One answer offered to these challenges by the field of chemistry is embodied by the ideas of *Green Chemistry* as a guiding framework for contemporary chemistry research, development, and industrial practice (Centi & Perathoner, 2009). Anastas and Warner in 1998 defined twelve principles for chemical processes, which are intended to reduce the impact of chemistry on the environment and resource consumption (Figure 1). Today, chemical research institutes and companies worldwide are looking for new synthesis pathways that incorporate the principles of Green Chemistry and sustainable development (Braun et al., 2006).

- Prevention
- Atom Economy
- Less Hazardous Chemical Syntheses
- Designing Safer Chemicals
- Safer Solvents and Auxiliaries
- Design for Energy Efficiency
- Use of Renewable Feedstocks
- Reduce Derivatives
- Catalysis
- Design for Degradation
- Real-time Analysis for Pollution Prevention
- Inherently Safer Chemistry for Accident Prevention

Figure 1: Short overview of the principles of green chemistry (Anastas & Warner, 1998)

In any case, sustainable development is not exclusively a task for chemistry, but is rather a challenge for all citizens. In a democratic society everyone is asked to contribute to sustainable development and to participate in the corresponding debates. For education this means that Education for Sustainable Development (ESD) is needed (Burmeister, Rauch & Eilks, 2012). Knowledge about sustainability is essential, because it enables students to assess information about new chemistry-based products and technologies in their lives and society at large. Development of corresponding skills is also unavoidable if we want our students to act appropriately and be able to effectively participate in societal debates today and in the future (van Eijck & Roth, 2007; Karpudewan, Ismail & Roth, 2012).

Chemistry education has different aims. Among them is learning about the societal dimension of science to prepare the next generation for future life and for participation in society (Hofstein, Eilks & Bybee, 2011). This perspective makes the societal dimension an essential component of all relevant science education (Stuckey, Hofstein, Mamlok-Naaman & Eilks, 2013). Society-oriented science education is relevant for students and the environment. It ensures that pupils can live as responsible citizens and react appropriately to challenges caused by science and technology (Fensham, 2004; Holbrook & Rannikmäe, 2007). Learning chemistry from an environmental and sustainability viewpoint makes chemistry teaching more meaningful and motivating, while at the same time increasing its value for general skills development in the sense of ESD (Burmeister & Eilks, 2012; Mandler et al., 2012; Robelia, McNeil, Wammer & Lawrenz, 2010).

Different ways have been suggested in the past to integrate sustainability into chemistry education at the secondary and undergraduate levels (Burmeister et al., 2012; Andraos & Dicks, 2012). However, implementation of ESD in chemistry education has still not been fully completed (Burmeister et al., 2012). Even though teachers' attitudes are generally promising, educators still feel that there is a continuing lack of appropriate teaching materials, learning scenarios and possible school experiments (Burmeister, Schmidt-Jacob & Eilks, 2013). This paper wants to contribute to closing this gap. It presents a case study discussing several different routes to synthesize vanillin. It also looks at how to learn from comparisons of the essential ideas behind green, more sustainable chemistry.

BACKGROUND

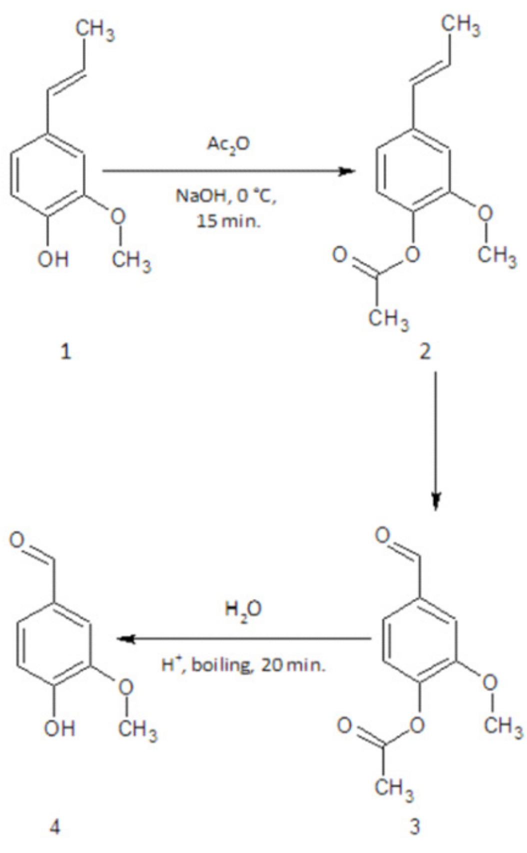
Vanilla belongs to the most oft-used food flavoring agents today. It is used in a wide variety of daily products. The main flavoring compound in natural vanilla is the compound vanillin (4-hydroxy-3-methoxybenzaldehyde). However, natural vanilla also contains only about 1-3% vanillin (Hocking, 1997), with the rest made up of over 130 various other organic compounds, which ensure the unique flavour of natural vanilla (Pérez-Silva et al., 2006).

Natural vanilla beans are grown mainly in Madagascar, the Comoros, and Reunion. About three-quarters of the annual harvest of about 2,000 tons are derived from these three islands and exported to the whole world (etcGroup, 2012). Worldwide demand of vanilla flavoring is, however, much higher than the supply. This is why many products include artificial vanillin instead of natural vanilla extracted from beans. Today, about 16,000 tons of synthetic vanillin are produced each year. It is not only a question of availability but also of price. Synthetic vanillin can be produced and purchased at a cost of about \$10-\$20 per kilogram, while natural vanilla extract reach prices of up to \$1,500 per kilo (Evolva, 2013).

Synthetic vanillin can be produced in various ways using different starting materials, mainly guaiacol, lignin and eugenol. Currently, the major commercial route for synthesizing vanillin is the condensation of guaiacol with glyoxylic acid, followed oxidation in an alkaline environment then decarboxylation (Kalikar, Deshpande & Chandalia, 1986; Huang, Du, Jiang & Ji, 2013). Another industrial process synthesizes vanillin from eugenol, a substance isolated from clove oil. Eugenol is isomerized and then oxidized by potassium permanganate or ozone (Lampman & Sharpe, 1983; Branan, Butcher & Olsen, 2007).

TWO SYNTHESIS ROUTES FOR VANILLIN

This paper will discuss two experiments inspired by well-known syntheses pathways for vanillin. The first is a synthesis of vanillin using conventional strategies by Lampman and Sharpe (1983). The second is a microwave approach used by Luu, Lam, Le and Duus (2009). These two pathways have been modified so that they can be conducted by upper secondary and undergraduate students in the classroom. The experiments can be carried out in a maximum of 4-5 hours. They can also be split up and carried out in a succession of shorter experimental phases. To save time, the isomerization of eugenol to isoeugenol was omitted and isoeugenol substituted as the starting material. The process involves acetylation, oxidative cleavage and hydrolysis. It employs no harmful chemicals. The entire procedure is summarized in Scheme 1.



Scheme 1: The Synthesis of vanillin from isoeugenol

Conventional synthesis of vanillin

Step 1- Acetylation of isoeugenol: Using protective groups is a fundamental concept in organic synthesis. Protective groups allow producers to achieve higher product yields and aid in avoiding unwanted by-products (Schelhaas & Waldmann, 1996). Addition of an acetyl group protects the hydroxyl group from oxidation in step 2. The protecting group is easy to introduce onto the molecule, quite stable, and easy to remove at the necessary time. A mixture of 3ml of isoeugenol **(1)** and 100ml of 1M sodium hydroxide solution are thoroughly combined in a beaker. After two minutes, crushed ice and 5ml of acetic anhydride are added to the solution drop for drop. The mixture is then stirred for 15 minutes, with the solids being separated at the end of this period. Purification of the crude isoeugenol acetate **(2)** is achieved by recrystallizing the solids in a 1:1 ethanol-water mixture. Typical student yields are generally 75-90%.

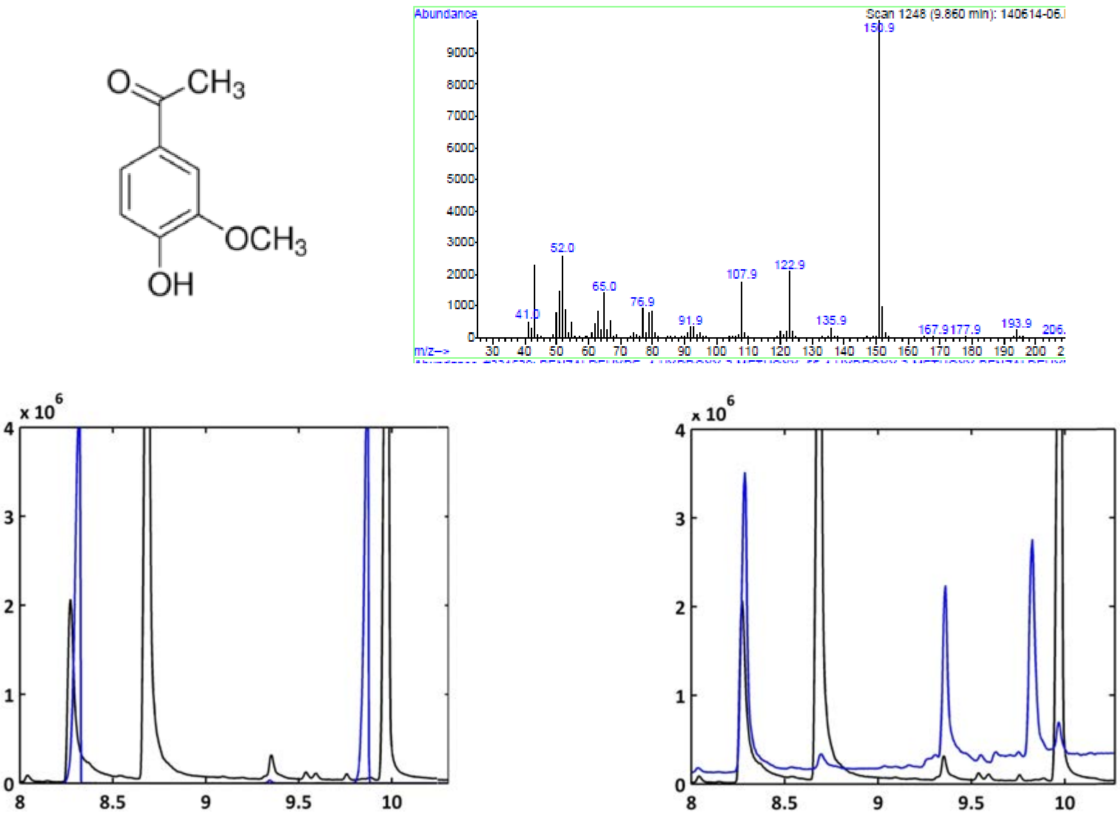
Step 2 - Oxidation of isoeugenol acetate: Oxidative cleavage is introduced by the addition of potassium permanganate as an oxidizing agent. Phase transfer catalysis is used so that over-oxidation of the product is kept to a minimum. 3.8g of potassium permanganate, 3.8g of manganese sulfate, 0.2g of benzyltriethylammonium chloride, 75ml of water and 75ml of methyl tert-butyl ether are mixed together in an Erlenmeyer flask without being heated. Benzyltriethylammonium chloride works as the phase transfer catalyst. Manganese sulfate is added to maintain pH-neutrality and also to reduce the chances that the acetyl protective group might be randomly removed by hydrolysis. 2g of isoeugenol acetate are slowly added over a time span of 5 minutes. The mixture is then stirred for an additional 15 minutes. The brown solid is removed and rinsed twice using 20ml of methyl tert-butyl ether. The aqueous and organic phases are then separated and the aqueous phase is again washed twice with 20ml of methyl tert-butyl ether. All of the organic layers are combined and the solvent is removed. Vanillin acetate **(3)** is obtained as a yellow oil, with typical yields roughly reaching the 40–50% range. Phase transfer catalysis is used to minimize over-oxidation. Nevertheless, the organic layer contains low quantities of vanillic acid. This undesired by-product can be eliminated by adding 1g of sodium hydrogen carbonate to the aqueous layer. After the reaction is over, 20ml of water are subsequently added and the two layers separated. The sodium salt of vanillic acid is located in the aqueous phase. The vanillin acetate remains in the organic layer.

Step 3 - Hydrolysis of vanillin acetate and purification: The protective acetyl group needs to be removed to obtain vanillin. The vanillin acetate is boiled with 30ml of half-concentrated hydrochloric acid under reflux for at least 20 minutes. The mixture is then cooled down to room temperature and an extraction is performed twice using 15ml of methyl tert-butyl ether. The organic phases contain vanillin (4). After removal of the solvent, final purification can be achieved by recrystallization of the crude vanillin in cyclohexane or water. In some cases, it may be beneficial to decolorize the solution with the help of activated carbon before allowing the vanillin to crystallize. Typical student yields are 40%.

Synthesis of vanillin using microwave technology

For a more sustainable chemistry synthesis, steps 2 and 3 of the synthesis can be altered. In this procedure, microwave technology is used instead of phase transfer catalysis. For this experiment, a laboratory microwave from MLS (Ethos 1600) is used. A mortar is used to thoroughly mix 10,6g of dry copper sulfate, 2,63g of potassium permanganate and 0,41g of isoeugenol, before they are placed in a sealable, microwaveable digestion vessel (MPV-100 *HT high performance PTFE container*, d= 3.5cm; h= 10cm). The well-sealed vessel is first left in the microwave for 5 minutes at 120 watts, then for an additional 15 minutes at 450 watts. After cooling, the reaction mixture is extracted two times using 15ml of methyl tert-butyl ether to obtain vanillin acetate. The solid is filtered off and the organic phase is collected separately. After the solvent has been removed, vanillin acetate **(3)** is obtained as a yellow oil. Typical student yields are around 50%. This method may also lead to overoxidation. To remove any undesired by-products, sodium hydrogen sulfate is used as described above. In the last step, acidic ion exchangers can be used as replacements for the half-concentrated acid and are generally quite practicable from a sustainability viewpoint.

The syntheses products can be detected using GC-MSD (figure 2a and 2b) or thin layer chromatography.



2a

2b

Figure2. Results of GC-MSD

DISCUSSION AND CONCLUSIONS

In a recent review of Education for Sustainable Development in chemistry education, Burmeister, et al. (2012) suggested that students be more thoroughly confronted with the issues of sustainable development and Green Chemistry in chemistry lessons. The paper suggests using different strategies to connect chemistry teaching with learning about both of these topics. These strategies range from (1) applying Green Chemistry principles in the educational science laboratory to (2) using sustainability issues to contextualize chemistry content learning, (3) employing technological and environmental challenges in a socio-scientific issues-based curriculum, and (4) using innovations in school life to introduce sustainability principles. Learning about the different syntheses pathways for vanillin has the potential to highlight the above-mentioned strategies. Green Chemistry principles are applied to the educational chemistry laboratory. Learning about different synthesis routes for vanillin contextualizes the essential methods of organic synthesis. Finally, reflection on the synthetic production of food additives can also lead to a socio-scientific discussion about the quality and availability of food, as well as bring the benefits and risks of intensive agriculture for the economy, society and the environment into better focus.

To date about 70 upper secondary school and undergraduate students have carried out the syntheses reactions described in this paper in an educational chemistry laboratory environment. The experiments have proven themselves suitable for demonstrating differing synthesis strategies in modern organic chemistry. The students enjoyed experiencing how diverse the synthesis of everyday products can be thanks to the wide array of innovative ideas for organic syntheses, including the microwave-induced variant discussed above. In the learning environment the two experiments were used to reflect about selected issues of Green Chemistry (Table 1).

Table 1: Discussion of the syntheses taking into account aspects of Green Chemistry: Comparison of the oxidation of isoeugenol acetate

	conventional procedure	using microwave technology
Principle 1 Waste production	The waste can be collected and subsequently quantified.	
	There are about 100ml of heavy metal-containing aqueous solution as a waste product. During the cleaning process additional waste water is produced.	There will be no aqueous waste. Only the oxidant is obtained as solid waste. Cleaning is easy: No additional aqueous waste is produced
Principle 2: Atom economy	Most by-products result from incomplete conversions in the reaction, which is necessary due to time constraints during school and undergraduate student experiments.	
	Apocynin is produced as an additional undesired byproduct, which lowers the economy of the reaction. The effective yield is roughly 40–50%	No additional byproducts. The real yield of the reaction is higher than with conventional synthesis. It is around 50%.
Principle 5: Solvents	Within the PTC, 75ml of methyl tert-butyl ether are required. In addition, 60ml of the solvent are necessary for subsequent extraction.	In order to separate the product from the catalyst, a total of only 30ml of methyl tert-butyl ether are used.
Principle 6: Energy requirment	The reaction mixture is not heated. Only a magnetic stirrer and a rotary evaporator are needed. However, in the full laboratory synthesis by Luu et al. (2009) the mixture should be heated for 90 minutes under reflux to achieve better yields.	The reaction mixture is heated for 20 minutes with a laboratory microwave. After the reaction, a rotary evaporator is also required. Thus, energy consumption is higher than in the conventional method if the mix is not heated under reflux for 90 minutes. Generally, microwave syntheses have advantages over conventional syntheses employing heating. Shorter reaction times are the result and lower energy consumption is possible.
Conclusion	Aspects of the waste production, the atom economy and the solvent usage result in an advantage of microwave technology. The conventional method for the preparation of isoeugenol acetate only has an advantage over microwave technology with respect to energy expenditure if the reaction mixture is not heated to improve yield.	

The alternate synthesis of vanillin falls more in line with the principles of Green Chemistry. The amount of necessary solvents has been reduced, concentrated acid can be replaced with a heterogenic catalyst, and less byproducts and waste are produced. Based on the context of vanillin synthesis learners can also be introduced to discussions about the complexity of production of everyday products and the impacts that these processes have on the economy and the environment.

ACKNOWLEDGEMENTS

We gratefully acknowledge the funding and support of the German Environmental Trust (Deutsche Bundesstiftung Umwelt).

BIBLIOGRAPHY

Andraos, J. and Dicks, A. P., Green chemistry teaching in higher education: a review of effective practices, *Chemistry Education Research and Practice* **13**, 69–79, 2012

Anastas, P.T. and Warner, J.C., *Green Chemistry: Theory and Practice*, Oxford University Press, Oxford, GB, 1998

Bradley, J.D, Chemistry education for development. *Chemistry Education International* **6**, [1], 2005, [URL: http://old.iupac.org/publications/cei/vol6/index.html. (August 2014)]

Branan, B.M., Butcher, J.T and Olsen, L.R., Using Ozone in Organic Chemistry Lab: The Ozonolysis of Eugenol. *Journal of Chemical Education* **84,** [12], 1979-1981, 2007

Braun, B., Charney, R., Clarens, A., Farrugia, J., Kitchens, C., Lisowski, C., Naistat, D. and O'Neil, A., Completing Our Education – Green Chemistry in the Curriculum, *Journal of Chemical Education* **83**, [8], 1126 – 1129, 2006

Burmeister, M., Rauch, F. and Eilks, I., Education for Sustainable Development (ESD) and chemistry education, *Chemistry Education Research and Practice* **13**, 59–68, 2012.

Burmeister, M. & Eilks, I., German Chemistry student teachers' and trainee teachers' understanding of sustainability and education for sustainable development, *Science Education International* **24**, 167-194, 2013.

Burmeister, M., Schmidt-Jacob, S. and Eilks, I., German chemistry teachers' understanding of sustainability and education for sustainable development—an interview case study, *Chemistry Education Research and Practice*, **14**, 169 – 176, 2013

Centi, G. and Perathoner, S., *Sustainable industrial processes,* Wiley-VCH, Weinheim, GER, 2009, p. 1-72.

etcGroup, *Synthetic Biology: Livelihoods and Biodiversity – Vanilla*, 2012. [URL: http://www.etcgroup.org/files/CBD_Vanilla_case_study_TA.pdf (August 2014)]

Evolva, *Evolva – Annual report 2012*, 2014. [URL: http://www.evolva.com/sites/default/files/attachments/evolva_annual_report_2012.pdf (August 2014)]

Fensham, P.J., *Defining an identity.* Kluwer, Dordrecht, NL, 2004.

Fisher, M.A., Chemistry and the Challenge of Sustainability, *Journal of Chemical Education* **89**, [2], 179–180, 2012

Hocking, M.B., Vanillin: Synthetic Flavoring from Spent Sulfite Liquor, *Journal of Chemical Education* **74**, [9], 1055-1059, 1997.

Hofstein, A., Eilks, I. and Bybee, R., Societal issues and their importance for contemporary science education: a pedagogical justification and the state of the art in Israel, Germany and the USA, *International Journal of Science and Mathematics Education* **9**, 1459-1483, 2011.

Holbrook, J. and Rannikmäe, M., The nature of science education for enhancing scientific literacy, *International Journal of Science Education* **29**, 1347-1362, 2007.

Huang, W.-B., Du, C.-Y., Jiang, J.-A. and Ji, Y.-F., Concurrent synthesis of vanillin and isovanillin, *Research on chemical Intermediates* **39**, 2849-2856, 2013.

Karpudewan, M., Ismail, Z. and Roth, W.-M., Ensuring sustainability of tomorrow through green chemistry integrated with sustainable development concepts, *Chemistry Education Research and Practice* **13**, 120–127, 2012.

Lampman, G.M. and Sharpe, S.D., A Phase Transfer Catalyzed Permanganate Oxidation, *Journal of Chemical Education* **60**, [6], 503-504, 1983.

Luu, T. x. T., Lam, T. T., Le, T. N. and Duus, F., Fast and Green Microwave-Assisted Conversion of Essential Oil Allylbenzenes into the Corresponding Aldehydes via Alkene Isomerization and Subsequent Potassium Permanganate Promoted Oxidative Alkene Group Cleavage, *Molecules* **14**, 3411-3424, 2009.

Mandler, D., Mamlok-Naaman, R., Blonder, R., Yayon, M. and Hofstein, A., High-school chemistry teaching through environmentally oriented curricula, *Chemistry Education Research and Practice* **13**, 80–92, 2012.

Pérez-Silva, A., Odoux, E., Brat, P., Ribeyre, F., Rodriguez-Jimenes, G., Robles-Olvera, V. and García-Alvarado, M. A., GC–MS and GC–olfactometry analysis of aroma compounds in a representative organic aroma extract from cured vanilla (*Vanilla planifolia* G. Jackson) beans, *Food Chemistry* **99**, 728-735, 2006.

Kalikar, R.S., Deshpande, R.S. and Chandalia, S.B., Synthesis of Vanillin and 4-Hydroxybenzaldehyde by a Reaction Scheme Involving Condensation of Phenols with Glyoxylic Acid, *Journal of Chemical Technology* **30**, 38-46, 1986.

Robelia, B., McNeill, K., Wammer, K. and Lawrenz, F., Investigating the impact of adding an environmental focus to a developmental chemistry course, *Journal of Chemistry Education* **87**, [2], 216–221, 2010.

Schelhaas, M. and Waldmann, H., Protecting Group Strategies in Organic Synthesis, *Angewandte Chemie International Edition* **18**, [35], 2056–2083, 1996.

Stuckey, M., Mamlok-Naaman, R., Hofstein, A., and Eilks, I., *The meaning of 'relevance' in science education and its implications for the science curriculum, Studies in Science Education* **49**, 1-34, 2013.

UNCED, *Agenda 21*, 1992. [URL: http://sustainabledevelopment.un.org/content/documents/ Agenda21.pdf (August 2014)]

van Eijck, E. and Roth, W.-M., Improving Science Education for sustainable Development, 2007. [URL: http://www.plosbiology.org/article/info%3Adoi%2F10.1371%2Fjournal.pbio.005 0306 (August 2014)]

World Commission on Environment and Development, *Our common future*, University Press, New York, USA, 1987.

Received 08-09-2014 /Approved 02 -11- 2015

A trial and evaluation of experimental kit of handy body-warmer through a model lesson on the rusting of iron

Un ensayo y evaluación de kit experimental a través de oxidación de hierro

Haruo Ogawa[1], Hiroki Fujii[2], and Akira Ikuo[1]

[1] Department of Chemistry, Faculty of Education, Tokyo Gakugei University, 4-1-1 Nukuikita-machi, Koganei-shi, Tokyo 184-8501, Japan, [2]Department of Science Education, Graduate School of Education, Okayama University, 3-1-1 Tsushimanaka, Kita-ku, Okayama 700-8530, Japan,
ogawah@u-gakugei.ac.jp

Abstract

Development and practice of a lesson model on the rusting of iron using an experimental kit of handy body-warmer through the principle of SEIC ("Special Emphasis on Imagination leading to Creation") and an evaluation of the use of the experimental kit were conducted. The lesson was carried out for undergraduate chemistry classes of junior (third year) level student in Tokyo Gakugei University (TGU). Students did an individual experiment actively and smoothly using the experimental kit with quite simple description of B6 size leaflet. Answers from students to questionnaire revealed that the individual experiment by use of the experimental kit was effective for realizing images of the phenomenon of rusting of iron and understanding the chemical reaction.

Key words: *experimental kit, individual experiment, imagination, SEIC, chemical education, lesson model*

Resumen

Se describe el desarrollo de la clase modelo de oxidación de hierro mediante el uso de un kit experimental a través del principio de la SEIC ("la imaginación que lleva a la creación") . Las clases se llevaron a cabo en el curso de química de pregrado (tercer año) en Tokio Gakugei University (TGU). Los estudiantes hicieron los ensayos individuales utilizando el kit experimental usando la simple descripción en un folleto especial. Las respuestas de los estudiantes en el